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ENGINEERING AND COST EFFECTIVENESS STUDY OF FLUORIDE EMISSIONS CONTROL

(FINAL REPORT)

JANUARY 1972

VOLUME I

Prepared under Contract EHSD 71-14
for
OFFICE OF AIR PROGRAMS
ENVIRONMENTAL PROTECTION AGENCY

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1. SUMMARY

This study, performed by RRI/TRW Systems for the Office of Air Programs of the Environmental Protection Agency, inventoried fluoride emission sources and investigated the technical and economic aspects of implementing soluble fluoride emission controls for major industrial sources. Soluble fluorides are defined as those fluorides with appreciably greater solubility (and ecological impact) than calcium fluoride.

Table 1-1 presents estimates of present and projected (year 2000) emissions of soluble fluorides from the major industrial process sources in the United States. Indications of the relative levels of confidence in the current estimates are included, as are projected emissions assuming that 99% emission control has been attained.

Table 1-2 presents current production rates and those projected for the year 2000. The evolution and emission factors for each process are presented in Table 1-3. The evolution factor includes all soluble fluorides leaving the process prior to control. The emission factor corresponds to that portion of the evolved soluble fluorides that eventually enters the atmosphere.

The following observations can be made after consideration of the information presented in the body of the report:

Five of the first six industries listed typically utilize no fluoride control (the exception is aluminum production).

It is technically possible to control soluble fluorides with available devices such as wet scrubbers; the immediate problem lies in implementation of that control, including collection of the evolved fluorides by hoods and similar effluent capture systems for treatment in the abatement devices.

Implementation of control involves a cost which reduces return on investment by varying amounts in different industries.

Control of fluoride emissions becomes largely a matter of economics and/or control regulations.

The lesser confidence attached to about half of the current emission estimates, including the top four processes in the current rankings of Table 1-1, indicates the need for more direct experimentally obtained data on both emissions and feed stock compositions for these industries.

The fluorides currently emitted may damage economic crops, farm animals, and materials of decoration and construction. It should be noted, however, that the potential for the observed ambient atmospheric levels to cause fluoride effects in man is negligible.

The major problem in measuring the fluoride contents of industrial effluent streams is that of obtaining representative samples which do not change by internal reaction prior to analysis. Current analytical techniques are satisfactory for laboratory analysis. No satisfactory continuous sampling and analytical system for continuous direct monitoring of process streams and stacks has been developed.

Research and development work is required to select control systems from those currently available which minimize the economic impact on a given industry, thereby making implementation of fluoride control as painless as possible.

Research and development work on fluoride contents of raw material feed stocks, process streams, and process/plant effluents is required to permit proper control design. Table 1-4 presents a summary of recommended research and development projects. Approximate total contract cost for the projects scheduled is estimated at $1.4 million.

Table 1-1. Soluble Fluoride Emissions (A)

	Current			Year 2000 With Current Practice		Year 2000 Assuming 99% Control Efficiency	
Ranking	Process	Emission Thousands Of Tons F Per Year (Yr)	Relative(F) Confidence	Process	Emission Thousands Of Tons F Per Year	Process	Emmission Thousands Of Tons F Per Year
1	Coal Burning For Power	27 (1970)	II	Primary Aluminum Manufacture	141	Primary Aluminum Manufacture	8.1
2	Open Hearth Steelmaking	25 (1968)	II	Coal Burning For Power	86	Coal Burning For Power	0.9
3	Iron Ore Sintering	18 (1968)	II	Iron Ore Pelletizing(B)	39	HF Production	0.7
4	Iron Ore Pelletizing(B)	18 (1968)	II	Expanded Clay Aggregate	25	Electrothermal Phosphorus	0.4
5	Primary Aluminum Production	16 (1970)	I	Wet Process Phosphoric Acid(C)	22	Iron Ore Pelletizing	0.4
6	Heavy Clay Products	10 (1968)	II	HF Alkylation(D)	16	Wet Process Phosphoric Acid(C)	0.3
7	Wet Process Phosphoric Acid(C)	6.4 (1970)	I	Heavy Clay Products	10	Triple Superphosphate(C)	0.3
8	HF Alkylation(D)	5.8 (1971)	I	Triple Superphosphate(C)	7.3	Expanded Clay Aggregate	0.3
9	Expanded Clay Aggregate	5.3 (1968)	II	Electrothermal Phosphorus	6.6	Defluorinated Phosphate Rock(C)	0.2
10	Normal Superphosphate	5.0 (1970)	I	Opal Glass Production	5.5	HF Alkylation	0.2
11	Electrothermal Phosphorus	4.1 (1968)	I	HF Production	5.3	Normal Superphosphate	0.1
12	Triple Superphosphate(C)	3.8 (1970)	I	Iron Ore Sintering	4.8	Heavy Clay Products	0.1
13	Opal Glass Production	3.3 (1968)	II	Defluorinated Phosphate Rock(C)	2.7	Opal Glass Production	<0.1
14	Blast Furnace	2.8 (1968)	II	Blast Furnace(E)	2.6	Iron Ore Sintering	<0.1
15	Defluorinated Phosphate Rock(C)	1.8 (1970)	I	Normal Superphosphate	1.4	Blast Furnace	<0.1
16	HF Production	0.7 (1970)	I	Enamel Frit Production	1.1	Ammonium Phosphate(C)	<0.1
17	Enamel Frit Production	0.7 (1968)	II	Cement Manufacture	0.8	Enamel Frit Production	<0.1
18	Copper Smelting and Refining	0.6 (1967)	III		1.6		<0.1
19	Ammonium Phosphate(C)	0.3 (1970)	I	Ammonium Phosphate(C)	0.8	Cement Manufacture	<0.1
20	Cement Manufacture	0.3 (1964)	II	Open Hearth Steelmaking	0	Open Hearth Steelmaking	0
21	Lead Smelting and Refining	0.2 (1967)	III		2.4		<0.1
22	Zinc Smelting and Refining	0.2 (1967)	III		2.4		<0.1
Total for Processes Considered		155.3			384.3		12.0

(A) Excludes CaF_2

(B) Assumes No Fluorspar Addition to Pellet

(C) Includes Prorata Allocation of Gypsum Pond Fluoride Emissions (Estimated as 6,300 Tons for 1970 and 21,000 Tons for 2000)

(D) Assumes 25% of Production Uses Lime Pit Disposal of Acid Sludges

(E) Assumes No Limestone Other Than That in Pellets or Sinter

(F) Relative Confidence Levels: I is Excellent; II is Good; III is Fair to Poor

Table 1-2. Production Trends to Year 2000

Product	Process	Present Production Million Tons/Year (year)	Year 2000 Production Million Tons/Year
Steel	Blast Furnace	130 (1968)(2)	120 (2)
	Iron Ore Sintering	50 (1968)(3)	13(3)
	Iron Ore Pelletizing	50 (1968)(3)	107(3)
	Open Hearth	66 (1968)	0
	Basic Oxygen	48 (1968)	135
	Electric Arc	16 (1968)	35
Phosphates as P_2O_5	Wet Process Phosphoric Acid (54%)	3.8 (1970)	13
	Ammonium Phosphate	2.4 (1970)	7.0
	Triple Superphosphate	1.4 (1970)	2.7
	Normal Superphosphate	0.7 (1970)	0.2
	Electrothermal Phosphorus	1.6 (1968)(4)	2.6(4)
	Defluorination of Phosphate Rock	0.09 (1970)(4)	0.14(4)
Aluminum	Prebake and Soderberg	4.0 (1970)	35
Cement	Wet and Dry Process	68 (1964)	200
Expanded Clay Aggregate		9.3 (1968)	44
Heavy Clay Products		24 (1968)	24
Coal	Power Generation	333 (1970)	1080
HF		0.34 (1970)	2.6
Alkylate	HF Alkylation	236,000 bbl/day (1971)	643,000 bbl/day
Enamel Frit		7,300 tons CaF_2(1) Utilized (1968)	11,800 tons CaF_2 Utilized
Opal Glass		34,500 tons CaF_2 Utilized (1968)	57,200 tons CaF_2 Utilized

(1) Expressed as tons of CaF_2 utilized in manufacture of product due to the varying compositions used.
(2) Expressed as ore tonnage in blast furnace burdens.
(3) Expressed as ore tonnage in process feed.
(4) Phosphate rock used in process feed as P_2O_5.

Table 1-3. Soluble Fluoride Evolution and Emission Factors by Process

	Evolution Factor		Emission Factor	
Industry and Process	LbF/Ton	Product	LbF/Ton	Product
Primary Aluminum Smelting				
Prebaked Anode	46	(Al)	6.94	(Al)
Horizontal Stud Soderberg	46	(Al)	10.12	(Al)
Vertical Stud Soderberg	46	(Al)	9.66	(Al)
Iron and Steel Manufacture				
Iron Ore Sintering	0.73	(Ore)	0.69	(Ore)
Iron Ore Pelletizing	0.73	(Ore)	0.69	(Ore)
Blast Furnace	0.088	(Ore)	0.065	(Ore)
Open Hearth Furnace	0.81	(Steel)	0.77	(Steel)
Basic Oxygen Furnace(a)	0	(Steel	0	(Steel)
Electric Arc Furnace(a)	0	(Steel)	0	(Steel)
Coal Combustion				
Electric Power Generation	0.16	(Coal)	0.16	(Coal)
Cement Ceramic and Glass Mfr.				
Opal Glass Production	21.8	(Glass)	21.8	(Glass)
Enamel Frit Production	3.15	(Dry Frit)	2.64	(Dry Frit)
Heavy (Structural) Clay Products	0.81	(Brick)	0.81	(Brick)
Expanded Clay Products	1.14	(Aggregate)	1.14	(Aggregate)
Portland Cement	0.008	(Cement)	0.008	(Cement)
Phosphate Rock Processing				
Wet Process Phosphoric Acid	4.07	(P_2O_5)(b)	3.36	(P_2O_5)(b)
Diammonium Phosphate	1.3	(P_2O_5)	0.23	(P_2O_5)(b)
Triple Superphosphate	21	(P_2O_5)	5.4	(P_2O_5)(b)
Normal Superphosphate	71	(P_2O_5)	14.2	(P_2O_5)
Electrothermal Phosphorus	30	(P_2O_5)	5.1	(P_2O_5)(b)
Defluorination of Phosphate Rock	210	(P_2O_5)	34	(P_2O_5)(b)
Non-Ferrous Metal Smelting and Refining				
Copper Smelting and Refining	0.78	(blister Cu)	0.78	(blister Cu)
Lead Smelting and Refining	0.34	(Lead)	0.34	(Lead)
Zinc Smelting and Refining	0.46	(Zinc)	0.46	(Zinc)
HF Alkylation Processes	0.18	(bbl alkylate)	0.15	(bbl. alkylate)
HF Production	52	(HF)	4.1	(HF)

(a) Estimated at zero soluble fluoride emission on the basis of thermodynamic equilibria analyses and the assumed total unavailability of hydrogen for conversion of other species to HF.

(b) Includes pro-rata allocation of gypsum pond fluoride emissions.

Table 1-4. Fluoride Emission Control - Recommended Research and Development (Projects by Industry)

Project Type / Industry	Ore Fluoride Content Characterization	Determination of Fate of F in Mfg. Process	Determination of Fate of Fluoride Evolved	Development of F Control Techniques	Determination of Fate of F in Control Process
Aluminum			1) Experimentally determine F capture by hoods and define building control requirements and characteristics		
Iron and Steel	1) Experimentally determine and verify average F contents of iron ore bodies and sinter/pellet plant charges for U.S. regional areas	2) Experimentally determine species and quantities of F compounds evolved and emitted by primary iron/steel production processes		3) Design, develop and test on bench and portable pilot plant economic, effective F emission control processes for iron/steel	
Coal Burning Steam-Electric Power	1) Experimentally determine area F, alkali, and alkaline earth metal contents and variabilities of coal	2) Experimentally determine the F species emitted by coal combustion as function of feed composition 4) Experimentally determine effect of SO_x and NO_x removal processes on fluorides in coal and effect of fluorides on processes			3) Experimentally determine quantities and types of F compounds removed by current and projected SO_2 control processes and effect on processes
Cement, Ceramic and Glass	1) Experimentally determine by U.S. regional areas the F contents of cement feedstocks 3) Experimentally determine the F content of feedstocks and process streams in frit mfr. 4) Experimentally determine by U.S. regional areas the F content of heavy clay product and expanded clay aggreg. feedstocks	2) Experimentally determine F species and quantities emitted in cement mfr. as function of feedstock F content			
Nonferrous metals	1) Experimentally determine the F contents of Cu Pb Zn ores and feedstocks by geographical area	2) Experimentally determine F species and quantities evolved and emitted in Cu Pb Zn smelting as functions of feed and process parameters			3) Experimentally determine the F species and quantities emitted from smelter byproduct H_2SO_4 plants as functions of process parameters and feeds

2. INTRODUCTION

This report presents the results of a study performed by Resources Research Incorporated and the Chemistry and Chemical Engineering Laboratory of TRW Systems Group under the direction of the Office of Air Programs, Environmental Protection Agency. Primary emphasis has been placed upon the determination of the engineering and cost effectiveness of control of soluble fluoride emissions from the major industrial sources. Soluble fluorides have been defined as those fluorine compounds which have a substantially greater solubility in water than calcium fluoride. Calcium fluoride emissions have to a large extent been deemphasized in the study because of their inert character and presumed lack of significant ecological and environmental impact. Other terms of special interest are evolution and emission. Evolution, as used in this report, includes all soluble fluorides evolved from a given process which would be discharged to the atmosphere if no control systems were utilized to reduce the quantity. Emission, as used in this report, includes only actual soluble fluoride discharges into the atmosphere, from a process in its current or projected state of emission control. Emission may equal evolution for those processes having no fluoride control, or may be lower by orders of magnitude where efficient control systems are employed.

Study tasks included inventory of fluoride emitting processes, process modeling, assessment of the state of the art of measurement and control technology, determination of control costs, projection of trends to the year 2000, and recommendations for research and development (R&D) activities to minimize soluble fluoride emissions in a cost effective manner. Performance of these tasks required evaluation of each industry processing significant quantities of fluoride-containing materials to determine the magnitude of fluoride evolution and emission, emission points, methodology available for measurement and control of emissions, and product costs with and without control. Obviously, this was a difficult task requiring definitive information about the specifics of various industrial processes. For many processes and industries, definitive information was not available. Many industries have not felt the need to concern themselves with fluoride emissions and have not allocated funds for acquiring emission data. Some industries, specifically phosphate rock processing and primary aluminum manufacture, have a high fluoride emission potential and are under significant pressure to minimize emissions. Industrial sources may or may not recognize that they have a potential fluoride emission problem, and they may or may not make emission data available if they exist. For each process considered in this study, emission data were gathered from public information, RRI experience, and results of other OAP studies. In cases where no data were available or data were so sketchy as to be without usefulness, emission factors were estimated based on raw material and product analyses, process chemistry, proprietory thermochemical equilibrium programs, information from consultants, and experience with similar products. In spite of the obvious uncertainty associated with estimates of emission factors, these estimates were necessary to prioritize emission sources and allow planning of future R&D activities to achieve maximum impact on the fluoride emission problem. Therefore, some assessment of the emission potential of each process under consideration was made to allocate resources logically to minimize the overall fluoride problem.

The following sections cover:

- Industry-by-industry descriptions of each production and control process of significance from a fluoride emission control standpoint; discussions of production trends extrapolated to the year 2000; process flow diagrams and mass balances for typical current plants; estimates of current and projected fluoride emissions; analyses of production and control process economics.
- Descriptions, cost estimates, priority assignments and schedules for the additional research and development programs recommended as the result of this study.
- Environmental and ecological effects of the emitted fluorides.
- Techniques for sampling, and measurement of fluoride pollutants in the various effluent streams.

- In appendix format — a general discussion of fluoride emission control devices; an inventory of pertinent industrial plants and their locations; tabulations of the physicochemical parameters of the evolved fluorides.
- The study bibliography.

3. INDUSTRIAL SOURCES

3.1 GENERAL

This section presents discussions of the fluoride emission control problem on an industry-by-industry basis. For each process emitting significant quantities of fluorides, production process models, projections, emission estimates, economic analyses, and fluoride control process models are described. The detail presented was sufficient to enable determination of the engineering and cost effectiveness of the currently employed control systems for soluble fluoride emissions - the stated objective of this study. This objective did not include provision of a basis for construction of facilities. The process descriptions, control systems, and economic analyses presented are therefore deliberately limited in scope and comprehensiveness to include only those elements necessary to estimate the cost associated with application of currently used devices to fluoride emission control, and its impact upon the profits obtained through sale of the various products manufactured. For two of the industries considered as fluoride sources, the phosphate rock processing and the primary aluminum reduction industry, specific studies are being conducted by CHEMICO and Singmaster and Breyer for EPA, the results of which should be available in 1972. Portions of their preliminary results are included in this report.

3.1.1 Economic Analyses - Discussion

All of the economic analyses performed for this study had the sole objective of determining the impact of the cost burden imposed by fluoride emission control systems upon the profitability of the basic manufacturing processes. The index selected to determine the impact was the relative change in return on investment (ΔROI) caused by the addition of emission control systems to manufacturing processes devoid of such pollution control devices. ΔROI was selected because of its relative lack of sensitivity to minor inaccuracies in determining cost of manufacture and to differences in accounting methods. These two points were deemed important because of the great variation in the accounting methods employed by the many industries involved, and because of the company-to-company and location-to-location deviations from the published manufacturing cost data for each production process.

Manufacturing Cost Economics. Return on investment for each production process or typical manufacturing complex was calculated from estimates of the total capital required (both construction and working capital) for the production system devoid of fluoride emission control devices; an assumed ratio of 20 to 80 for debt to equity capital*; yearly "f.o.b. costs" which were the sum of annual manufacturing costs plus an assumed average 2% general and sales cost burden; annual gross income; and a 50% tax rate on profit. Estimates of total capital required and manufacturing costs were based upon data available from the literature and from TRW files, and upon the assumptions listed in Table 3-1.

As an example of ROI calculations, consider a 120,000-ton per year primary aluminum plant. The ROI is calculated from the following:

90 $MM total capital
72 $MM equity capital (80% of total capital)
51.2 $MM/year f.o.b. costs (50.2 $MM/year manufacturing costs plus 1.0 $MM/year for general and sales expense at 2%)
69.6 $MM/year gross income
50% tax rate

Thus, ROI is generally,

$$\text{ROI} = 12.8\% = \frac{0.5 \times (69.6 \text{ \$MM/year} - 51.2 \text{ \$MM/year}) \times 10^2\%}{72 \text{ \$MM}}$$

The difference between the ROI before and after requiring fluoride pollution control equipment divided by the ROI before pollution control is termed (for this study), as the relative percent decrease in ROI (ΔROI). Capital for the pollution control equipment is added to the plant capital for the final ROI and ΔROI calculations. For our example, if the aluminum plant

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*Applicable only to production equipment and plant systems. For the purposes of this study, pollution control equipment was assumed to be completely equity capital funded.

Table 3-1. Manufacturing Process Economics Assumptions*

- Base years for cost data(1)

Phosphate Rock Industries:	1966	Opal Glass:	1970
Power Plant:	1969	Expanded Clay:	1969
HF Production:	1969	Structural Clay:	1968
Aluminum:	1969	Portland Cement:	1970
Steel:	1970		

- "Battery Limits" include the means of production usually represented by the flow sheet.

Electric Power	$0.007 per kwh/hr
Cooling Water	$0.03 per M gal
Boiler Feed Water	$0.25 per M gal
Operating Labor	$4.00 to $5.00/man-hr
Labor Overhead	30 percent of operating labor and supervision
Maintenance and Supplies	6 percent of investment/yr
Depreciation	10 percent of investment/yr
Plant Overhead	70 percent of operating labor and supervision
Taxes and Insurance	3 percent of investment per year
Supervision and Benefits	100 percent of operating labor (supervision 20 percent, fringe benefits 80 percent)
Interest (Investment and/or work capital)	Not included
Distribution and Sales Cost	Not included
Start-Up Costs	Not included
General and Administrative Costs	Not included
Storage	Where specified
Operating Rate	100 percent capacity, 330 days per year
Offsites	20-60 percent of investment
Contingency	10 percent

- Offsites (where applicable)

Water supply treatment and cooling
Solids handling
Docks
Office Buildings
Yard Piping
Yard Electrical
Maintenance Equipment
Trucks and Tractors
Furniture
Tanks
Paving
Compressors
Waste Disposal
Piling
Concrete
Insulation
Structural
Oil Storage
Boiler
Worker Housing

*Exceptions are indicated on the individual process sheets.

(1) CE plant cost index was used to standardize costs to January 1971.

experiences a 12.8% ROI before installation of fluoride control equipment and a 9.7% ROI after installation, the ΔROI is 24.2%. It should be noted that ΔROI is very sensitive to the installed capital. For example, if the installed capital is decreased by using indirects and contingency of 10% and 10% instead of 15% and 20%, the ΔROI reduces to 12% from 24.2%.

In general, smaller facilities experience a somewhat larger decrease in ROI relative to larger facilities. This means that they will find it more difficult to finance new control equipment.

Control Cost Economics. The process control economic analysis uses an incremental cost approch. Capital and operating costs are added to the uncontrolled process economics for those items which are necessary for fluoride pollution control, but are not required for manufacturing. For example, maintenance costs for the control equipment are included but operating labor is not. The extra operating labor would be minimal and it is assumed that the regular operating personnel would assume these duties.

Presented in the following paragraphs is a brief description of the cost estimating procedure for the fluoride pollution control systems. The control process economic analysis is based on the pollution control model presented for the plant size, flows and process conditions listed under the various "Uncontrolled Process Model" diagrams and mass balances.

The economic analysis contains the following cost elements: (1) capital charges, (2) total operating cost and (3) total pollution control cost in units of dollars per hour (or dollars per heat) and dollars per ton of product.

Equipment cost (f.o.b.) of the control device is the primary input to the economic analysis. The f.o.b. equipment cost at the required capacity is obtained from vendor quotes, industry survey and correlations or published cost curves. In the situations where the equipment cost quote is for a different capacity than required, the conventional relationship is used,

$$C_2 = C_1 \, (V_2/V_1)^K$$

where

C_2 = cost of equipment at the new capacity (V_2)
C_1 = cost of equipment at quoted capacity (V_1)

K factors for the various equipment types employed in this analysis are presented in Table 3-2.

Auxiliary materials required to install the equipment and installation labor costs are added to the f.o.b. equipment costs. Auxiliary materials include foundations, electrical conduit, piping, valves, instrumentation, and such other permanently installed materials as are required for installation of the primary control device. Installation labor includes all labor necessary for installation. For most preliminary economic analyses, these costs may be estimated by "field installation factors" published in the literature. These factors usually run between 1.5 and 3.0 times the f.o.b. equipment costs and are presented in the economic section after each piece of equipment.

The installation factor as presented in the control process economics is defined by the following expression,

$$\text{Factor} = \frac{\text{Installed Cost}}{\text{Equipment Cost}}$$

This definition will tend to give a low value for the factor since the "actual installed factor" is based on the cost of the equipment constructed of carbon steel. The special construction materials costs (usually neoprene-lined steel) are added to the equipment cost but do not increase the installation costs. For example, a pressure vessel 4 feet in diameter by 6 feet in tangent height has a base cost (carbon steel) of about $2300. Assuming a field installation factor of 4.23 and in this case, a monel-clad adjustment factor of 3.89, the total installed cost is given by

Table 3-2. Scaling Factors (K)

Equipment	Range	K
Fan	1.5-4.0 (Mcfm)	.68
Cyclones		
Heavy Duty	4-28 (Mcfm)	.82
Light Duty	2-15 (Mcfm)	.87
Multiple	1-19 (Mcfm)	.80
Multiple (In Combination with Low Voltage Precipitator)	1-19 (Mcfm)	.83
Electrostatic Precipitator	10-2,000 (Mcfm) (Note A)	.647
Spray Scrubber	(Note B)	.60-.65
Wet Scrubber	(Note B)	.60-.65
Spray Chamber	(Note B)	.60-.65
Floating Bed Scrubber	(Note B)	.60-.65
Spray Towers	(Note B)	.60-.65
Quench Tower	(Note C)	-
Thickener	-	.7
Vacuum Filter	10-2,200(ft^2)	.78
Venturi Scrubber	8-100 (Mcfm)	.50
Cyclonic Clarifier	100-10,000 (gpm)	.73
Waste Heat Boiler	100-10,000 (ft^2)	.65
Secondary Exchanger	100-10,000 (ft^2)	.65
Bag House	10-2,000 (Mcfm)	.68
Water Cooled Duct	-	.65
Spark Box	-	.6
Dry Alumina Adsorption Process	-	.6
Spray Screen	18-96 (ft^2)	.97

Notes

(A) The size, installed cost, operating cost and maintenance cost for a "turn-key" single stage industrial electrostatic precipitator were calculated from actual installed cost correlations provided by a precipitator supplier. Installed cost includes flues, support steel, fan, stack, low voltage wire and conduit, cooling tower, pressure and temperature controls, dust handling system and foundations. The precipitator requires particle sizes greater than two microns and a loading greater than 0.1 grains/ft^3 (1.43×10^{-5} lbs/ft^3). Electrical conductivity of particles must be between a good conductor and a good insulator or resistivity must be between 10^4 and 10^{10} ohm-cm. Sizing requires the capacity (10-2,000 Mcfm), required efficiency (90-99%), a precipitation constant (between 0.05 and 0.50) and knowledge of the stream velocity. Additional required information includes the current Chemical Engineering Plant Cost Index (C.I.), classification of the gas as corrosive or non-corrosive, and the voltage (E).

Correlations

Operating Cost ($/hr) = 0.0006 x (cfm) x 0.007

Maintenance Cost = 1300$ per year to 8000$ per year

(B) Installed costs are estimated from graphs presented in the Guthrie article. The primary sizing parameters are the diameter and height (costs are most sensitive to diameter). The diameter is calculated from the gas flow (cfm) and the allowable gas velocity. Height is calculated on an individual case (depending on scrubber type) from data supplied by equipment manufacturers.

(C) Quench tower cost from private sources; data is for the actual capacity required; no scale factor was used.

Equipment Cost (EC) = Base Cost x Material Factor

Installation Cost (IC) = Base Cost x (installation factor - 1)

Installed Cost (\$) = Equipment Cost + Installation Cost

or

EC = \$2300 x 3.89 = \$ 8,947

IC = \$2300 x (4.23-1) = \$ 7,429

\$ = \$8,947 + \$7,429 = \$16,376

Note that although the carbon steel installation factor is 4.23, the factor for monel steel is

$$\text{Factor} = \frac{\text{installed cost}}{\text{equipment cost}} = \frac{\$16,376}{\$\ 8,947} = 1.83$$

Project indirect costs are added to the total pollution control system and represent items such as sales taxes, U. S. freight, packing, insurance, ocean freight, import duties, temporary facilities, small tools, project engineering, fees, procurement, etc. Indirect costs vary considerably from project to project. For this analysis, an indirect charge of 10% is assumed for the total installed equipment cost (Reference 4386). The 10% is composed of 3% contractor's fees, 2% engineering and 5% construction expenses. An "on-going" company will usually have an existing engineering department which implies additional engineering requirements should be minimal. Thus a minimal engineering expense was selected. Contingency is taken as 10% of capital (Reference 4386). Contingency may range between 5-15% (Reference 4386) and one reference takes it as 34% of capital (Reference 4383). Since the control systems utilize known technology, 10% was selected and is probably on the "High" side. Note, that an incremental approach was taken in this analysis, that is, only costs were included in the control economic estimates that are in addition to normal production costs. For example, corporate engineering is not considered since it is already taken as a part of the overhead in the uncontrolled process model.

The capital charge is taken as the fraction of capital per year which corresponds to the straight line depreciation schedule permitted for the industry by the U. S. Internal Revenue Service in June, 1971. Start-up costs and interest on the investment during construction were not capitalized in order to make control process economics consistent with uncontrolled production economics.

Operating costs were calculated on an item by item basis. That is, operating cost corresponding to the operation of a unit is calculated and charged to that unit. For example, if a dry multiple cyclone cleans 60,000 cfm at 68^{0}F with an inlet dust-loading of 5 grains/cu ft, its operating cost is estimated by knowing its pressure drop; 4.3 in w.g. pressure drop (Reference 4387). The following relationship gives the required horsepower (Reference 4388).

$$\text{Horsepower} = \frac{0.0158 \times \text{cfm} \times \text{Wg}}{e}$$

where

cfm = volume at temperature in cubic feet per minute

Wg = pressure or suction in inches water gage

e = percent fan efficiencies

or

$$\text{Horsepower} = 68$$

For most initial economic analyses, the operating costs for a limited number of pumps may be omitted (such as in the control system case). As a worst case example, a wet high energy venturi with a capacity of 60,000 cfm uses an eleven horsepower pump to feed the required 480 gpm. The operating cost for the pump is less than $.06 per hour. This is insignificant when compared to the $2.68 per hour operating cost for the 31.5 in. w.g. pressure drop in the gas stream.

The following cost factors for maintenance were utilized in determining operating costs.

Unit	$ Per Year
Bag House	10,000
Cyclone	1,000
Cyclonic Clarifier	1,000
Cyclonic Spray Tower	1,000
Electrostatic Precipitator	3,000
Fan	3,600
Floating Bed Scrubber	2,000
Lime Pit	3,000
Liquid Solid Separator	500
Quench Tower	1,600
Radiant Cooling Coils	800
Secondary Heat Exchanger	800
Liquid Solid Separator	400
Spray Chamber (Scrubber or Tower)	2,000
Spray Screen	2,500
Spark Box	1,000
Thickener	500
Vacuum Filter	2,600
Venturi Scrubber	1,000
Venturi Separator	1,000
Waste Heat Boiler	870
Water Cooled Duct	800
Wet Cyclone	1,000
Wet Scrubber	2,000

CONTROL PROCESS ECONOMICS

FOOTNOTES

(1) Includes piping, concrete, steel, instruments, electrical, insulation, paint, etc., site preparation and installation labor.

(2) Includes project engineering, process engineering, design and drafting, procurement, temporary facilities, construction equipment, insurance, sales and other taxes, etc.

(3) Supplied by steelmaking furnace.

(4) Assuming 25 prebaked anode, or horizontal stud Soderberg cells per electrostatic precipitator.

(5) Assuming 10 prebaked anode or horizontal stud Soderberg cells per scrubber.

(6) Includes the liquid-solid separator cost.

(7) Included in the installed capital cost.

(8) Assuming 10 prebaked anode or vertical stud Soderberg cells per control process.

(9) Assuming a 50,000 tpy horizontal stud Soderberg plant and 15 cells per tower.

(10) Includes the cost of the liquid-solid separation unit.

(11) Assuming a 50,000 tpy prebaked anode or vertical stud Soderberg plant.

(12) Includes reactors, fans, alumina handling equipment, site preparation and indirects.

(13) Includes power and maintenance and a net credit for recovery of reusable material.

(14) Assumes a 50,000 tpy plant.

(15) Includes liquid solid separation unit.

(16) Assuming an initial cost of $50,000 and 0.5 men to maintain it (at $6000 per year).

(17) Pollution control costs could be reduced to 3.40 + 2.00 $/ton Al if fluoride credit is taken and if larger electrostatic precipitators are used.

(18) At 0.007 $/kwhr.

(19) 200 tons per heat; 12 heats per day.

(20) The size, installed cost, operating cost and maintenance cost for a "turn-key" single-stage industrial electrostatic precipitator were calculated from correlations provided by a precipitator supplier. Installed cost includes flues, support steel, fan, stack, low voltage wire and conduit, cooling tower, piping, pressure and temperature controls, dust handling system and foundations. The precipitator requires particle sizes greater than 2 microns and a loading greater than 0.1 grain/ft^3 (1.43×10^{-5} lb/ft^3). Electrical conductivity of particles must be between a good conductor and a good insulator or resistivity must be between 10^4 and 10^{10} ohm-cm. Sizing requires the capacity (10-2,000 Mcfm), required efficiency (0 to 99%), a precipitation constant (between 0.05 and 0.50) and knowledge of the stream velocity. Additional required information includes the current Chemical Engineering Plant Cost Index (C.I.), classification of the gas as corrosive or noncorrosive, and the voltage (E).

Correlations

Operating Cost (\$/hr) = 0.0006 x (cfm) x 0.007

Maintenance Cost = 0.63 \$/hr for noncorrosive gas
1.00 \$/hr for corrosive gas

(21) At \$0.02 /1000 gal.

(22) At \$0.50 /ton.

(23) Company private design information.

(24) 200 tons per heat; 10 hours per heat, 2 heats per day.

(25) \$6.20/ton $Ca(OH)_2$.

(26) Furnace capacity 75 tons/heat; 4 heats per day.

3.1.2 Thermochemical Analysis Approach

As indicated in Section 1, significant uncertainty is associated with determination of the evolution and emission rates from many of the processes of interest. In the absence of definitive experimental data, an analytical approach based on thermodynamic equilibrium calculations was utilized.

TRW has applied its proprietary Chemical Analysis Program (CAP) to evaluation of pollutants from a number of high temperature processes, such as combustion of coal, manufacture of glass, and smelting of iron and steel. The desirability of this analytical approach was fourfold. First, in cases where experimental measurements of pollutant output were not available, the calculated values provided a basis for evaluating the pollution potential of the process or industry considered. Second, even when experimental data were available for a given process output, the chemical composition of the pollutant stream was, on occasion, not measurable, e.g., both HF and SiF_4 were measured and reported as gaseous fluoride, and trace components, possibly toxic, were not measured at all. The CAP provided a component by component breakdown including trace components. Third, where only limited data were available, the theoretical approach was employed to verify or modify the conclusions on fluoride evolution. Fourth, consideration of the formation mechanisms of the various pollutants yielded valuable information on potential abatement and control strategies.

All equilibrium calculations were performed using TRW's proprietary Chemical Analysis Program with thermochemical data derived from JANAF and similar high quality sources. Because of the complexity of the chemical systems under consideration (over 300 possible gaseous and over 100 possible condensed species) the analyses were performed on various combinations of the systems elements to derive the final product distribution. All analyses performed contained, however, the basic components as defined in the various input mass balances. The nitrogen was replaced in the analyses by helium after initial calculations indicated no production of trace element nitrogen compounds from the nitrogen in the air or coal.

Illustrative of the CAP approach to a particular problem is the analysis of coal combustion in power plants. The primary objective was to calculate the forms and quantities of fluorides evolved. A secondary objective was to determine the fate of heavy metal constituents and their potential as toxic emissions. The results of this evaluation, as well as those for opal glass manufacture and the smelting of iron and steel, are presented in the text of the report.

3.2 PRIMARY ALUMINUM SMELTING INDUSTRY

3.2.1 General

Primary aluminum production is both a present and a projected major source for soluble fluorides emitted to the atmosphere. The fluorides emitted are mainly gaseous hydrogen fluoride (HF), particulate cryolite (Na_3AlF_6) and aluminum fluoride (AlF_3). Virtually all of the soluble fluorides emitted by the industry come from the reduction process, which thus merits detailed examination.

This section covers those general considerations for which the primary aluminum smelting industry may be considered as an entity. Such considerations include: reduction technology; current and projected levels of soluble fluorides discharged to the atmosphere; current and projected production levels; fluoride emission control systems; and the impact of fluoride emission control systems on return on investment (ROI).

3.2.2 Industry Description

Aluminum is manufactured by the electrolytic reduction of alumina (Al_2O_3) dissolved in a molten salt bath. The molten salt "bath" is composed of cryolite (Na_3AlF_6) and various salt additives. The electrolysis is performed in a carbon crucible, housed in a steel shell, using the crucible as cathode, and using carbon anodes. The reduction cells are referred to as "pots," and there are three basic types of pot in use today. These are the prebake (PB), the horizontal stud Soderberg (HSS), and the vertical stud Soderberg (VSS). Figure 3-1 illustrates the three cell types.

As indicated by Figure 3-1, the three pot types differ chiefly in their anode configurations. The prebaked anode cell, as indicated by its name, employs a replaceable, consumable carbon anode, formed by baking prior to its use in the cell. Both Soderberg pots employ continuously formed consumable carbon anodes where the anode paste is baked by the energy of the reduction cell itself.

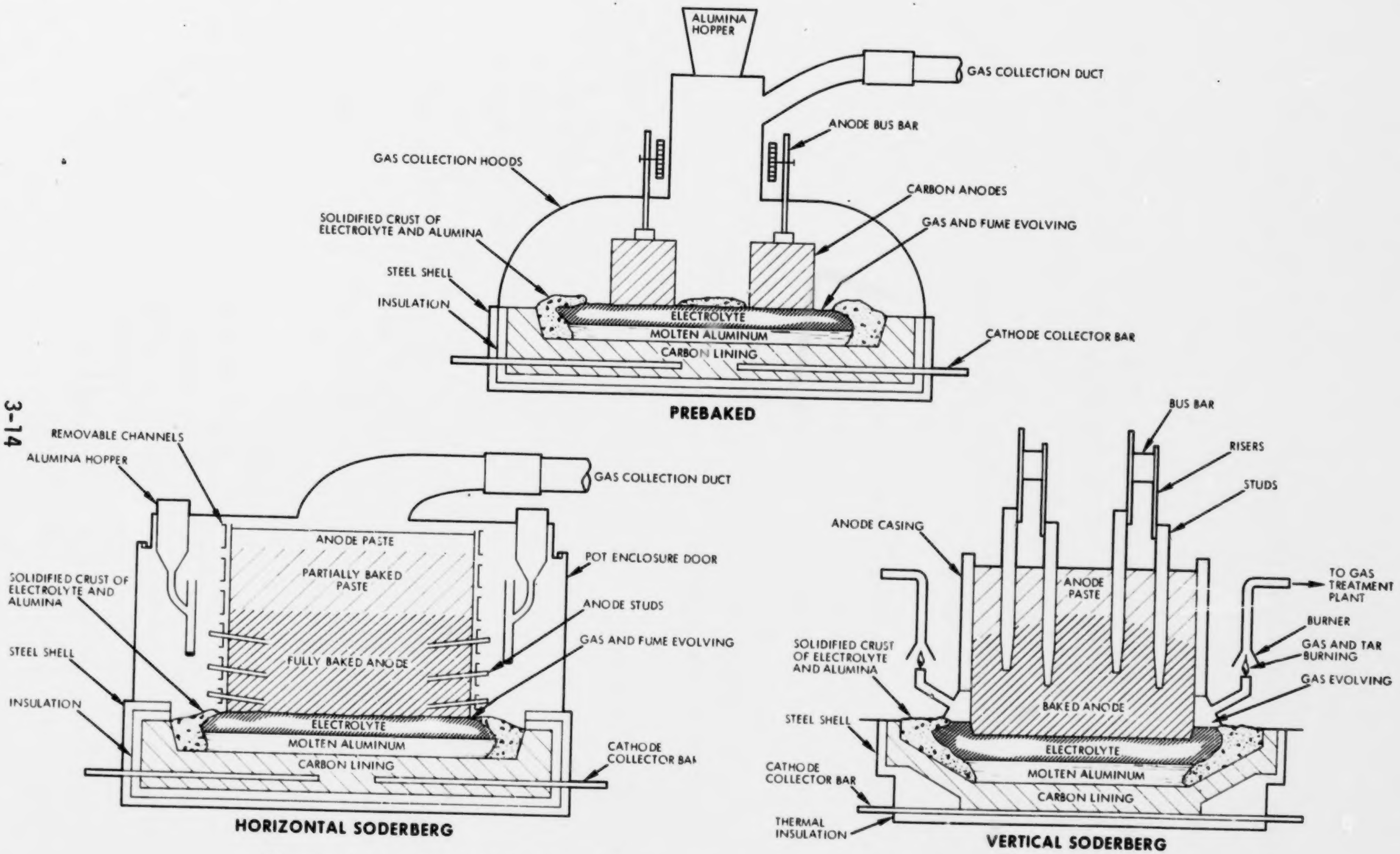

ALUMINA HOPPER
GAS COLLECTION DUCT
ANODE BUS BAR
GAS COLLECTION HOODS
CARBON ANODES
SOLIDIFIED CRUST OF ELECTROLYTE AND ALUMINA
GAS AND FUME EVOLVING
STEEL SHELL
INSULATION
ELECTROLYTE
MOLTEN ALUMINUM
CARBON LINING
CATHODE COLLECTOR BAR
PREBAKED
REMOVABLE CHANNELS
ALUMINA HOPPER
GAS COLLECTION DUCT
ANODE PASTE
POT ENCLOSURE DOOR
PARTIALLY BAKED PASTE
SOLIDIFIED CRUST OF ELECTROLYTE AND ALUMINA
ANODE STUDS
GAS AND FUME EVOLVING
STEEL SHELL
FULLY BAKED ANODE
INSULATION
ELECTROLYTE
MOLTEN ALUMINUM
CARBON LINING
CATHODE COLLECTOR BAR
HORIZONTAL SODERBERG
BUS BAR
RISERS
STUDS
ANODE CASING
ANODE PASTE
TO GAS TREATMENT PLANT
BURNER
SOLIDIFIED CRUST OF ELECTROLYTE AND ALUMINA
GAS AND TAR BURNING
GAS EVOLVING
BAKED ANODE
STEEL SHELL
ELECTROLYTE
CATHODE COLLECTOR BAR
MOLTEN ALUMINUM
CARBON LINING
THERMAL INSULATION
VERTICAL SODERBERG

Figure 3-1. Details of Prebaked and Soderberg Aluminum Reduction Cells

Present American production practice makes extensive use of prebake cells and horizontal stud Soderberg cells. Although the Soderberg cell was hailed as an economic advance when developed, currently, the trend in new plant design is to use the prebake cells because of operating difficulties associated with condensed tars from the volatilization of Soderberg anode paste pitch.

The "pot" contains both the molten electrolyte (bath) and molten aluminum. The bath, composed, as noted above, of cryolite and additives, is less dense than the molten aluminum. Because of this, the molten aluminum collects as a layer of liquid in the bottom of the cell. The function of the molten cryolite layer is threefold — to act as an electrolyte, to dissolve the alumina charged to the cell, and to protect the aluminum from the atmosphere. Bath temperature is approximately 950°C. During production, the carbon of the anode is oxidized (about 0.45 to 0.55 pound per pound aluminum) by the oxygen released from alumina in electrolysis, but the carbon of the cathode is not oxidized. Detailed information describing the production of aluminum is available in Reference 4164.

The source of fluorides emitted to the atmosphere by aluminum reduction is the fluoride electrolyte which contains cryolite, AlF_3, and fluorspar. Cryolite can be represented as a complex of $3NaF \cdot AlF_3$. For this molecular proportion, the weight ratio of NaF to AlF_3 is 1.50. In practice, this ratio is maintained in the range of 1.36 to 1.43 by addition of Na_2CO_3, NaF, or AlF_3. The alumina feed material contains about 0.25% Na_2O (Reference 4164) which results in a continuing requirement for AlF_3 addition in normal cell operation to hold the ratio in the operating range. Fluorspar is added to the bath to depress the freezing point of cryolite and allow operation at lower temperatures than would otherwise be possible. Usage of fluoride containing electrolyte ranges from 0.03 to 0.10 pound/pound aluminum.

A portion of the feed fluorides evolves from the pot as both gaseous and particulate material. At the same time, the pot lining absorbs fluorides which may be recovered after the useful life of the pot is expended (about 3 years). The amount of fluoride absorbed in the linings has apparently not been accurately determined and reported. It is estimated by TRW as approximately 50% of the total input fluoride based on conversations with aluminum industry personnel.

Effective capture of the off-gases and fumes for subsequent cleaning is the most difficult single technical problem. Two approaches to this problem have been taken. The first approach, typical of U.S. practice, utilizes a hood over each pot to collect the fumes evolved. However, hoods must allow access for operations in the pot such as ore addition, anode replacement, and aluminum removal. Thus, a portion (frequently fairly large) of the off-gases escapes into the pot-line building and then escapes to the atmosphere through the building roof ventilators (monitors) (Reference 4288). In some cases, the monitor output is controlled in addition to the hood output. A need exists for hood systems that will capture the fumes and gases evolved while minimizing the ingested air to allow cleaning at high efficiency and minimum cost.

The second approach, used to a minor extent in the U.S. and more frequently in European practice, allows free flow of the pot fumes into the pot room and utilizes the monitor system to capture the entire flow of room ventilation air including the fumes. This approach requires about ten times as much air to be processed as the hood system and sometimes results in higher fluoride exposures for the workers.

Raw material and energy requirements for aluminum production are presented in Table 3-3. These values vary slightly from plant to plant, but they are generally consistent with modern practice.

3.2.3 Production Trends

The aluminum industry is a major current source of atmospheric fluorides. The expansion of reduction facilities at planned and existing plants will increase these emissions to a level which will make this industry the prime emitter of fluorides by the year 2000. Some aluminum reduction processes under development would present no fluoride problem; however, there is no indication that any proposed new process will come into wide service in the next several decades, if at all (Reference 4288).

Table 3-3. Raw Material and Energy Requirements for Aluminum Production

Amperes through pot line	60,000 - 225,000
Voltage drop per cell	4.3 - 5.2
Current efficiency, percent	85 - 90
KWH/pound aluminum	6.0 - 8.5
Pounds Al_2O_3/pound aluminum	1.89 - 1.92
Pounds fluoride electrolyte/pound aluminum	0.03 - 0.10
Electrode carbon, pound/pound aluminum	0.45 - 0.55

It can be stated with reasonable certainty that U.S. primary aluminum production will increase at least threefold between now and 1984. Most major producers expect to reach this projection. A recent survey found projected growth rates to range from a high of 9.5 percent to a low of 4.8 percent annually through 1980 (Reference 4250). Other sources indicated rates of 6.4 percent (Reference 4289) and 7.0 percent (Reference 4290) through 1980. If an expected value of 7.4 percent (Reference 4250) is extrapolated to the year 2000, the production of aluminum will increase from 4.0 million tons (Reference 4290) (1970) to 35 million tons. Year 2000 projections may be seen in Table 3-4. Current and projected production rates for each of the three basic processes are shown in Table 3-5.

Table 3-4. Estimated Future Electrolytic Aluminum Production

	1947	1967	Past 20-Year Annual Growth Rate (A)	2000 (B)	Estimated Year Annual (B) Growth Rate
U.S. Population	144.1 MM (C)	199.1 MM	1.7%	336.2 MM	1.6%
GNP (constant 1967 dollars)	356.8 MMM	785.1 MMM	3.9%	3.15 MMMM	4.3%
Primary Aluminum Production	0.57 MM tons	3.27 MM tons	9.1%	34.5 MM tons	7.4%
Total Consumption	0.95 MM tons	4.15 MM tons	7.7%	38.7 MM tons	7.0%
Per-Capita Consumption	13 lb	42 lb	5.8%	230 lb	5.2%

(A) Growth rates are compunded annually.

(B) Data extrapolated from 1984 projections given in Reference 4250.

(C) M represents 1000 -- MM represents 1,000,000, etc.

The projections in Table 3-5 are based on the assumption that the actual percentages produced by each process will remain the same during the period 1970 to 2000. While this may seem inconsistent with the current trend toward installation of PBA facilities noted below, past experience in the aluminum industry indicates that extrapolation of trends can lead to possibly erroneous conclusions on which single technology would become predominant. As an example, the prior strong American trend to Soderberg cells, which still predominate in Europe, went through a reversal in 1970. In 1970, 38% of the U. S. aluminum reduction capacity employed the Soderberg electrode - a drop from 46% in 1965 - with only 10% of the new capacity planning to use it.

To avoid erroneous conclusions, it was considered a reasonable compromise to project the current distribution to the year 2000. Requirements for air pollution control may strongly influence the actual distribution practiced by the industry.

Table 3-5. Aluminum Production

Production Process	Percent of Total Aluminum Production	1970 Aluminum Production (million tons/year)	Estimated(A) Aluminum Production in 2000 (million tons/year)
PB	61.9%	2.48	21.7
HSS	25.5%	1.02	8.9
VSS	12.6%	0.51	4.4
Total	100.0%	4.01	35.0

(A)Assumes no change in 1970 process distribution

A significant factor not connected with demand that could easily lower the projected U.S. output would be a move by U.S. producers to add primary capacity outside of the U.S. -- near bauxite deposits, for instance -- in order to reduce costs, and then import the resultant metal. If world tariffs continue to decline, this would appear to become more and more attractive. Also, constantly increasing labor costs could force producers to move outside the U.S.

3.2.4 Fluoride Control and Emissions Summary

Both gaseous and particulate fluorides are evolved from the electrolytic cells producing aluminum. Dry dust collection devices (centrifugal collectors, miltitube cyclones, or electrostatic precipitators) and/or wet scrubbers may be used as control devices. Individual pot hoods are "ganged" (manifolded) to feed the control devices. When the hood access panels are opened, the air flow into the hood system may be insufficient to prevent escape of gas and particulates from the cell into the pot room. Hood capture efficiencies may drop to levels much below the normal operating range. Individual hood exhaust flow rates range from 1000 to 5000 cubic feet per minute per cell.

Scrubbing equipment commonly employed in aluminum manufacture includes redwood scrubbing towers, floating bed scrubbers, and wet cyclonic scrubbers. In addition, the Aluminum Company of America (ALCOA) has developed a dry adsorption process for the collection and recovery of reduction cell fluorides (Reference 323). The process exposes the alumina feed to the pots to the evolved fumes. The fluorides adsorb on the alumina and are returned to the pots. A baghouse is used to prevent solids loss. Efficiency is reported to be about 97- to 99% for both gaseous and particulate fluorides. Although ALCOA has developed and patented their particular "398" process, the use of alumina as a dry adsorbent in other equipment configurations has been studied previously. There is some question about the effect of tars on the dry adsorption process, buth ALCOA reports that it is suitable for both prebake and Soderberg cells.

Roof monitor scrubbers were not considered in detail in this study since they represent a minority usage and the trend in the industry is expected to be toward more efficient pot hoods.

Controlled process models for each of the three processes are presented in the individual process description sections.

Soluble fluorides evolved from the primary aluminum smelting processes averaged 46 pounds (as F) per ton of product in 1970 (Reference 4208). This corresponds to an annual fluoride evolution rate of 92,200 tons in 1970. The soluble fluoride emission factor for the year 1970 for the aluminum reduction plants averaged 8.1 pounds (as F) per ton of product aluminum (Reference 4208), equivalent to the annual discharge of 16,230 tons (as F) of soluble fluorides to the atmosphere. The ranges of data presented in the referenced OAP Study appear to be consistent with those of the other data sources analyzed and to include a much greater portion of the American industry in the data base. It must be noted, however, that the source of the data was an industry questionnaire which probably does not represent emissions during less than optimum conditions.

Projections for the year 2000 indicate that, if current control practice continues, 141,000 tons (as F) per year of soluble fluorides will be emitted to the atmosphere by the aluminum reduction plants. This would be by far the largest industry source of soluble fluoride pollutants. If improvements in control practice to achieve 99 percent control are adopted by the industry, the projected emissions of soluble fluorides for the year 2000 would drop to 8,050 tons (as F). Table 3-6 presents the process and industry current totals and projections. For fluoride emission values from various cell types, the basic data utilized was that of Reference 4208, an interim report dated May 10, 1971 by Singmaster and Breyer on the aluminum industry. These data are subject to change since the Singmaster and Breyer program is not completed.

Dust evolution from handling of raw materials is not considered in detail in the above analysis because the magnitude is small (about 1 to 6 pounds fluorine/ton aluminum), the emission control devices are relatively efficient, and the environmental effect is low. Much of the dust may settle in the plant and be recovered, thereby not constituting an emission to the surroundings.

Table 3-6. Fluoride Emissions From Aluminum Production Processes

Process	1970 (A) Soluble Fluoride Emissions (10^3 tons F /Year)	2000 (B) Soluble Fluoride Emissions Current Control Practice (10^3 tons F /Year)	2000 (B) Soluble Fluorides Emitted with 99% Control Technology (10^3 tons F /Year)
PB (C)	8.61	75	4.99
HSS	5.16	45	2.05
VSS	2.46	21	1.01
Total	16.23	141	8.05

(A) Total Al production was 4.01 million tons annually in 1970.

(B) Projected Al production of 35 million tons annually reflecting an expected growth rate of 7.4%.

(C) Includes prebaked anode furnace emissions.

3.2.5 Process Description

3.2.5.1 Prebaked Anode Aluminum Production

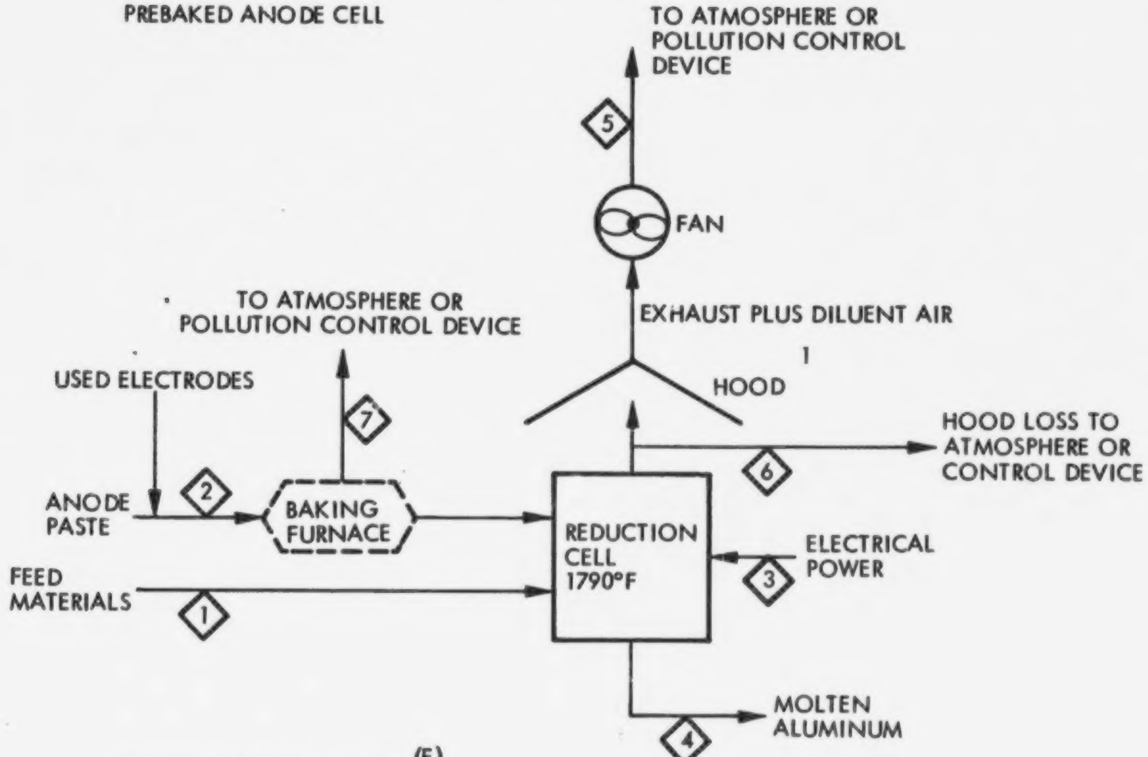
Present and Future Production Levels. Aluminum is currently produced by the prebaked anode process at 19 locations (including those under construction) throughout the U. S. A detailed listing of these locations can be found in Appendix 7.2. The prebaked anode process will grow in production level from 2.48 million tons of aluminum in 1970 to 21.7 million tons in 2000.

Process Description. As noted earlier, the important difference between prebake and Soderberg cells is the method of replacing spent anode. For prebaked anode cells, prior to utilization in the reduction cell, anode paste is solidified to block form in a separate baking furnace. These individual blocks of carbon--typically 14 to 24 per cell--attached to metal rods serve as replaceable anodes. These burn away at a rate of about an inch per day. Spent anode assemblies are removed on a rotating basis, usually two at a time.

An uncontrolled process model of the prebaked anode reduction process is shown in Figure 3-2. The mass balance is based on an 89% hood capture efficiency (actual experience as reported in Reference 4208). The balance of fluoride not shown is allocated to cathode absorption.

Fluoride Emission Control Techniques. The fluoride emission control techniques employed are illustrated in the flow diagrams and mass balances, Figures 3-3 and 3-4 for the prebaked anode cell and the prebaked anode furnace control systems, respectively. For cell effluent control, process C is currently most prevalent but process D shows promise of greater acceptance in the future. For baking furnace effluent, processes A and B are generally used in combination, in series.

Fluoride Emissions. As shown in Table 3-6, the prebake anode process currently (1970) emits 8610 tons of fluoride annually corresponding to about 53% of the total from the industry. This emission level reflects an industry-wide average for prebake anode process fluoride abatement of 85%. If expected production levels arereached in the year 2000, the emission from this source will be 75,000 tons (as F^-) annually, assuming extension of current control practice. If 99% control efficiency technology is utilized industry-wide, the fluoride emitted from this source would be about 5000 tons annually.



PREBAKED ANODE CELL

TO ATMOSPHERE OR POLLUTION CONTROL DEVICE
5
FAN
EXHAUST PLUS DILUENT AIR
1
HOOD
HOOD LOSS TO ATMOSPHERE OR CONTROL DEVICE
6
TO ATMOSPHERE OR POLLUTION CONTROL DEVICE
7
USED ELECTRODES
ANODE PASTE
2
BAKING FURNACE
REDUCTION CELL 1790°F
ELECTRICAL POWER
3
FEED MATERIALS
1
MOLTEN ALUMINUM
4

1. HOOD EFFICIENCY IS 89% (E)
(AVERAGE OF OLD AND NEW
PREBAKE ANODE CELLS)

A

BASIS - 2070 lb ALUMINUM PRODUCED PER DAY PER AVERAGE PREBAKE ANODE CELL

PROCESS STREAMS - LBS/HR.

Material	Stream Number						
	1	2	3	4	5*	6*	7*
HF					$1.09^{(D,B)}$	.09(g)	$.04(g)^{(E)}$
Na_3AlF_6	$2.5(s)^{(C)}$				.73(s) $^{(D,B)}$ as F	.13(s) as F	
AlF_3	$3.3(s)^{(C)}$						
Total Fluoride$^{(F)}$	5.8						.04
Total as F$^{(F)}$	3.6				1.77	.21	.04
Alumina	165				1(s)	.1(s)	
Anode Material as C		50					
Aluminum				86			
CO_2					170(g)	17(g)	
H_2O					1(g)	.05(g)	
C					.2(s)	.01(s)	
Electrical Power			660/KWH				
Approx. Total Stream	170	50	-	86	$170^{(A)}$	17	$.04^{(B)}$

* Gaseous effluent stream

(A) Plus 215,000 SCFH of diluent air (STP = 32°F, 14.7 psia)

(B) Plus other exhaust gases from prebake oven

(C) Ref. 4250

(D) Ref. 4254

(E) Ref 4208

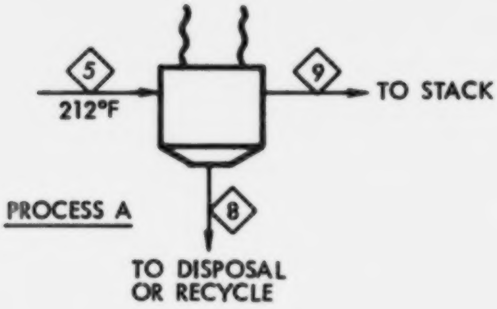
(F) The balance not shown is cathode absorption of electrolyte

Soluble F Evolution Factor = 46 lb F/ton Aluminum Produced$^{(E)}$

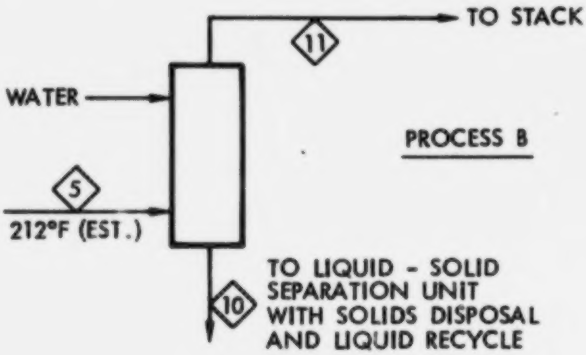
13

Figure 3-2. Electrolytic Aluminum Production--Prebaked Anode Cell, Uncontrolled Process Model

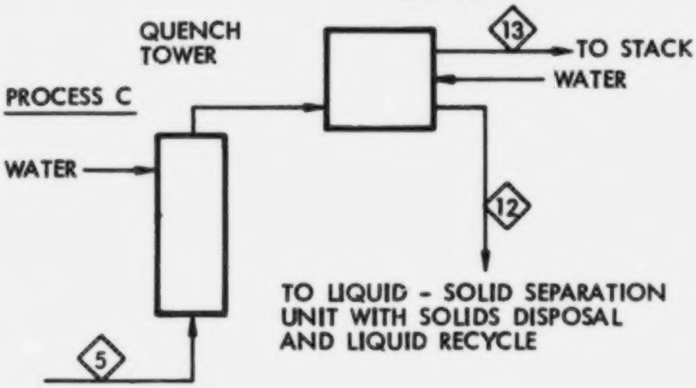
ELECTROSTATIC PRECIPITATOR
EFF. = 98% PARTICULATE
0% GASEOUS (ASSUME NO ADSORPTION)


5
212°F
9
TO STACK
PROCESS A
8
TO DISPOSAL
OR RECYCLE

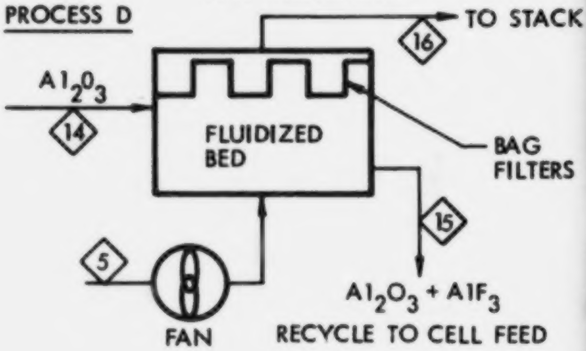
FLOATING BED SCRUBBER
EFF. = 72% PARTICULATE
95% GASEOUS


TO STACK
11
WATER
PROCESS B
5
212°F (EST.)
TO LIQUID - SOLID
SEPARATION UNIT
WITH SOLIDS DISPOSAL
AND LIQUID RECYCLE
10

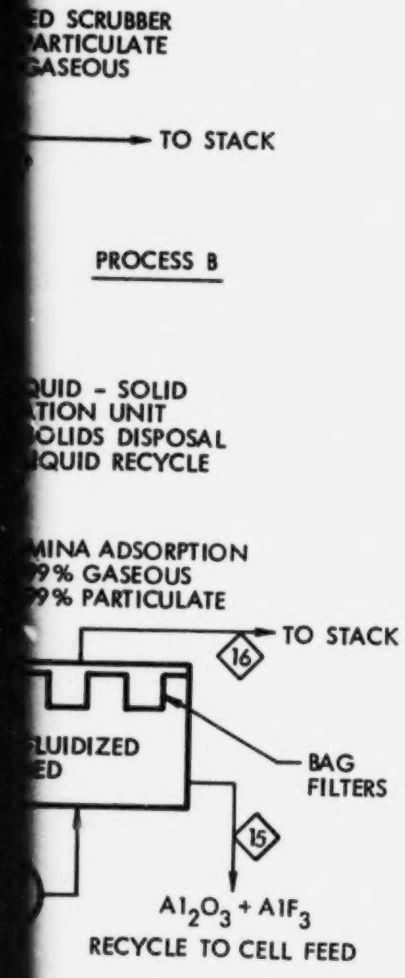
SPRAY SCREEN
EFF. = 83% PARTICULATE
96% GASEOUS


QUENCH
TOWER
PROCESS C
13
TO STACK
WATER
WATER
12
TO LIQUID - SOLID SEPARATION
UNIT WITH SOLIDS DISPOSAL
AND LIQUID RECYCLE
5

DRY ALUMINA ADSORPTION
EFF. = 99% GASEOUS
99% PARTICULATE


PROCESS D
TO STACK
16
Al_2O_3
14
FLUIDIZED
BED
BAG
FILTERS
5
FAN
15
$Al_2O_3 + AlF_3$
RECYCLE TO CELL FEED

A


ED SCRUBBER
PARTICULATE
GASEOUS
TO STACK
PROCESS B
QUID - SOLID
ATION UNIT
OLIDS DISPOSAL
IQUID RECYCLE
MINA ADSORPTION
99% GASEOUS
99% PARTICULATE
TO STACK
16
FLUIDIZED
ED
BAG
FILTERS
15
$Al_2O_3 + AlF_3$
RECYCLE TO CELL FEED

BASIS - 2070 LBS. ALUMINUM PRODUCED PER DAY P

PROCESS STREAMS - LBS./HR.

Material	Stream					
	5	6*	8	9*	10	11*
HF	1.09(g)	.09(g)		1.09(g)		.06(g)
Na_3AlF_6 AlF_3	.73(s) as F	.13(s) as F	.715(s) as F	.015(s)$^{(C)}$ as F	.53(s) as F	.20(s) as F
Total as F	1.77	.21	.715	1.06	.53	.26
Alumina	1(s)	.1(s)	.98(s)	.02(s)$^{(C)}$	.72(s)	.28(s)
CO_2	170(g)	17(g)		170(g)		170(g)
H_2O	1(g)	.05(g)		1(g)		400(g)
C	.2(s)	.01(g)	.196(s)	.004(s)$^{(C)}$	.14(s)	.06(s)
Approx. Total Stream	170$^{(A)}$	8	1	170$^{(A)}$	1$^{(B)}$	570$^{(A)}$

*Gaseous Effluent Stream

(A) Plus 215,000 SCFH Diluent Air (STP = 32°F, 14.7 psia)

(B) Plus Water and Soluble Fluorides

(C) Ref. 4208

Source	Calc. Soluble Flu	
	Process A	Pro
Treated Hood Exhaust Emission	24.65	
Untreated Hood Loss to Atmosphere	4.88	
Total Emission to Atmosphere from Cell	29.53	1

Reported Average Overall Prebake Anode Cell Soluble Fluor

(Reflects the utilization of series abatement systems by

3

2070 LBS. ALUMINUM PRODUCED PER DAY PER PREBAKED ANODE CELL

PROCESS STREAMS - LBS./HR.

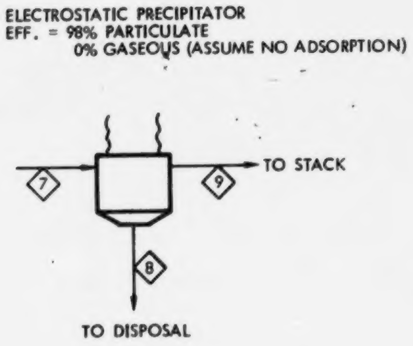
	Stream Number							
	9*	10	11*	12	13*	14	15	16*
s)	1.09(g) .015(s)$^{(C)}$ as F	.53(s) as F	.06(g)$^{(C)}$ .20(s)$^{(C)}$ as F	.61(s) as F	.04(g)$^{(C)}$ .12(s)$^{(C)}$ as F		1.75(s)$^{(C)}$ as F	.01(g)$^{(C)}$ .007(s) as F
	1.06	.53	.26	.61	.16		1.75	.017
)	.02(s)$^{(C)}$	.72(s)	.28(s)$^{(C)}$	.83(s)	.17(s)$^{(C)}$	20(s) (Est)	21(s) (Est)	.01(s)$^{(C)}$
	170(g)		170(g)		170(g)			170(g)
	1(g)		400(g)		400(g)			1(g)
s)	.004(s)$^{(C)}$	.14(s)	.06(s)$^{(C)}$	.17(s)	.03(s)$^{(C)}$		.198(s)	.002(s)$^{(C)}$
	170$^{(A)}$	1$^{(B)}$	570$^{(A)}$	1$^{(B)}$	570$^{(A)}$	20	21	170$^{(A)}$

14.7 psia)

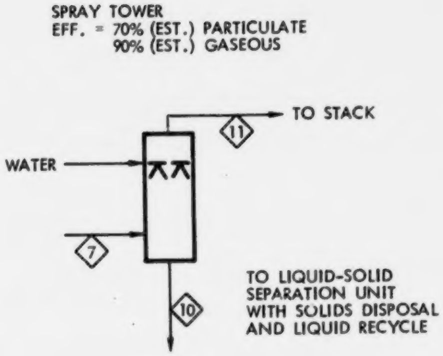
	Calc. Soluble Fluoride Emission Factor = lb F/ton Al			
urce	Process A	Process B	Process C	Process D
Exhaust	24.65	6.04	3.72	0.40
d Loss to	4.88	4.88	4.88	4.88
n to Atmosphere	29.53	10.92	8.60	5.28

Overall Prebake Anode Cell Soluble Fluoride Emission Factor = 6.94 lb F/ton Al$^{(C)}$
ization of series abatement systems by a significant portion of the industry)

Figure 3-3. Electrolytic Aluminum Production - Controlled Process Model Prebaked Anode Cell


ELECTROSTATIC PRECIPITATOR
EFF. = 98% PARTICULATE
0% GASEOUS (ASSUME NO ADSORPTION)
7
9
TO STACK
8
TO DISPOSAL

PROCESS A


SPRAY TOWER
EFF. = 70% (EST.) PARTICULATE
90% (EST.) GASEOUS
TO STACK
11
WATER
7
10
TO LIQUID-SOLID
SEPARATION UNIT
WITH SOLIDS DISPOSAL
AND LIQUID RECYCLE

PROCESS B

BASIS - 2070 LB ALUMINUM PRODUCED PER DAY PER PREBAKED ANODE CELL BAKING FURNACE

PROCESS STREAMS - LB/HR

Fluoride Balance Only Material	Stream Number				
	7	8	9*	10	11*
HF	.04(g)	0	.04(g)(Est)		.004(g)(Est)
$HF \cdot XH_2O$				.036(l)(Est) as F	
Total Fluoride	.04	0	.04	-	.004
Total as F	.04	0	.04	.036	.004
Approx. Total Stream	.04(A)	0(B)	.04(A)	.036(C)	.004(A)

* Gaseous Effluent Stream

(A) Plus other exhaust gases from the baking furnace.

( ) Plus non-fluoride particulate

(C) Plus water and non-fluoride particulate.

Fluoride Emission Factor
Process A - 0.93 lb F/ton AC
Process B - 0.09 lb F/ton AC

Average Overall Baking Furnace Soluble Fluoride Emission Estimated to be 0.5 lb F/ton Al.

Figure 3-4 Electrolytic Aluminum Production - Controlled Process Model, Baking Furnace, Prebaked Anode Cell

3.2.5.2 Horizontal Stud Soderberg Aluminum Production

Present and Future Production Levels. In 1970, the horizontal stud Soderberg process accounted for 25.5% of the total domestic aluminum production. This corresponds to a total of 1.02 million tons annual production from eight production sites located within the U. S. A detailed summary of these facilities is presented in Appendix 7.2.

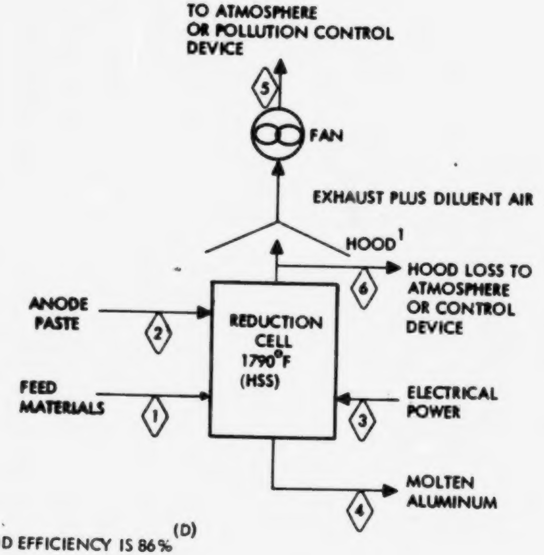
Projected aluminum production levels for the year 2000 for the horizontal stud Soderberg process are 8.9 million tons of annual production.

Process Description. The horizontal stud Soderberg cell uses a continuous anode. A mixture of pitch and carbon aggregate called "paste" is added at the top of the superstructure periodically, and the entire anode assembly is moved downward as it burns away. The result of baking the paste in place is to add heavy organic material (tars) to the cell effluent stream.

In the horizontal stud Soderberg (HSS) cell, the anode is contained by aluminum sheeting and steel channels. The channels are perforated with holes about 3 inches in diameter, and the "studs" or electrode connections are inserted through these holes into the anode while it is 3 feet or so above the molten bath and is still fairly soft. The anode is baked solid in the region just above the molten bath by heat from the process. As the anode is lowered, the bottom channel is removed after the lower row of studs is pulled out and the flexible electrical connectors are moved to a higher row. This process requires significant mechanical manipulation with the hood door open thereby reducing hood capture efficiency.

An uncontrolled process model of the HSS cell is presented in Figure 3-5. The mass balance is based on an 86% hood capture efficiency

HORIZONTAL STUD SODERBERG CELL


TO ATMOSPHERE OR POLLUTION CONTROL DEVICE
5
FAN
EXHAUST PLUS DILUENT AIR
HOOD¹
6
HOOD LOSS TO ATMOSPHERE OR CONTROL DEVICE
ANODE PASTE
2
REDUCTION CELL 1790°F (HSS)
FEED MATERIALS
1
3
ELECTRICAL POWER
4
MOLTEN ALUMINUM

1. HOOD EFFICIENCY IS 86%(D)

BASIS - 2070 lb ALUMINUM PRODUCED PER DAY PER HSS CELL

PROCESS STREAM - lbs/hr

Material	Stream Number					
	1	2	3	4	5*	6*
HF					1.06 (g) (C,D)	.11 (g)
Na_3AlF_6 AlF_3	2.5 (s)(B) 3.3 (s)(B)				.69 (s)(D) as F	.17 (s) as F
Total Fluorides Total as F	5.8(E) 3.6(E)				1.70	.28
Alumina	165				1 (s)	.1 (s)
Anode Mat'l. as C		50				
Aluminum				86		
CO_2					160 (g)	27 (g)
H_2O					1 (g)	.1 (g)
C					.2 (g)	.02 (g)
Electrical Power			660 KWH			
Approx. Total Stream	170	50	--	86	160(A)	27

* Gaseous Effluent Stream

(A) Plus 250,000 SCFH of diluent air

(B) Ref. 4250

(C) Ref. 4254

(D) Ref. 4208

(E) The balance not shown is cathode adsorption of electrolyte

Soluble F Evolution Factor = 46 lb F/ton Aluminum Produced(D)

Figure 3-5. Electrolytic Aluminum Production - Uncontrolled Process Model, Horizontal Stud Soderberg Cell

(actual experience reported in Reference 4208). The balance of the fluoride not shown is allocated to cathode absorption of electrolyte.

Fluoride Emission Control Techniques. The controlled process models and mass balances for the HSS process are presented in Figure 3-6. Predominant usage is Process C, Principal problem areas are blockage of equipment by tar buildup and low fluoride collection efficiency due to the decreased hood capture efficiency noted above.

Fluoride Emissions. Soluble fluoride emission from the horizontal stud Soderberg was 5160 tons (as F^-) in 1970 (Reference 4208). This is equivalent to about 32% of the fluoride emitted industry-wide and is based on an industry-wide HSS process fluoride abatement efficiency of 78% (Reference 4208). The emission level will increase to 45,000 tons (as F^-) in the year 2000 if current projected production levels are reached and if current control efficiency is maintained. If 99% control technology is utilized industry-wide, the fluoride emission level from this process will drop to 2050 tons annually.

3.2.5.3 Vertical Stud Soderberg Aluminum Production

Present and Future Production Levels. Four facilities in the U. S. (see Appendix 7.2) currently utilize the vertical stud Soderberg process in the production of aluminum. They accounted for 0.51 million tons--12.6% of the total production--in 1970. Projected production levels are 4.41 million tons of aluminum produced via the VSS process in the year 2000. These data are presented in Table 3-5.

Process Description. The vertical stud Soderberg is similar to the horizontal stud Soderberg with the exception that the studs are mounted vertically instead of horizontally in the cell. The studs must be raised and replated periodically but that is a relatively simple process. The tar problem is alleviated as discussed below. The uncontrolled process model of the VSS is presented in Figure 3-7. The mass balance is based on an 80% hood

BASIS - 2070

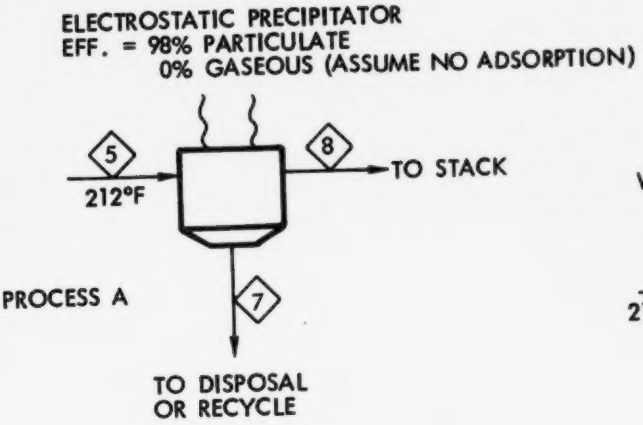
Material
HF
Na_3AlF_6
AlF_3
Total as F
Alumina
CO_2
H_2O
C
Approx. Total Stream

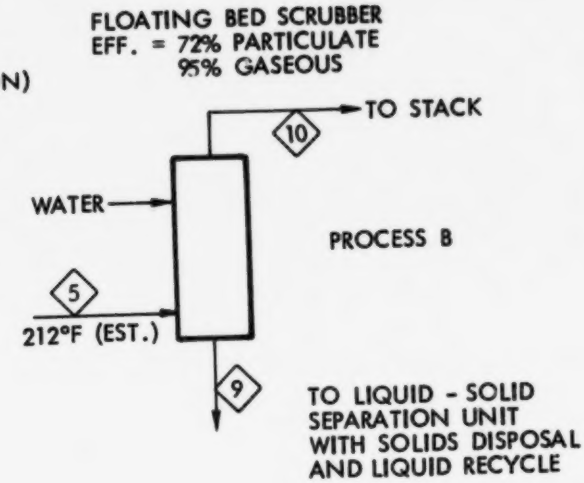
*Gaseous Effl

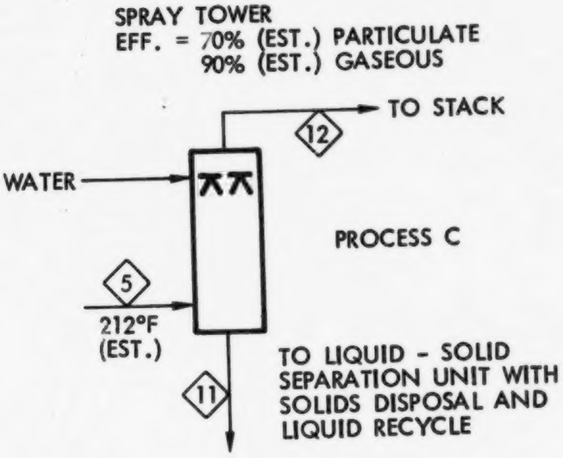
(A) Plus 250,

(B) Plus solu

(C) Ref. 4208


ELECTROSTATIC PRECIPITATOR
EFF. = 98% PARTICULATE
0% GASEOUS (ASSUME NO ADSORPTION)
5
212°F
8
TO STACK
7
PROCESS A
TO DISPOSAL OR RECYCLE


FLOATING BED SCRUBBER
EFF. = 72% PARTICULATE
95% GASEOUS
10
TO STACK
WATER
PROCESS B
5
212°F (EST.)
9
TO LIQUID - SOLID SEPARATION UNIT WITH SOLIDS DISPOSAL AND LIQUID RECYCLE


SPRAY TOWER
EFF. = 70% (EST.) PARTICULATE
90% (EST.) GASEOUS
12
TO STACK
WATER
PROCESS C
5
212°F (EST.)
11
TO LIQUID - SOLID SEPARATION UNIT WITH SOLIDS DISPOSAL AND LIQUID RECYCLE

A

BASIS - 2070 lb ALUMINUM PRODUCED PER DAY PER HORIZONTAL STUD SODERBERG CELL

PROCESS STREAMS - LB/HR

Material	Stream Number							
	5	6	7	8*	9	10*	11	12*
HF	1.06(g)	.11		1.06(g)		.05(g)$^{(C)}$		.11(g)(Est)
Na_3AlF_6	.69(s)	.17(s)	.68(s)	.01(s)$^{(C)}$	.50(s)	.19(s)$^{(C)}$	.48(s)	.21(s)(Est)
AlF_3	as F	as F	as F	as F	as F	as F	as F	as F
Total as F	1.70	.28	.68	1.02	.50	.24	.48	.31
Alumina	1(s)	.1(s)	.98(s)	.02(s)$^{(C)}$	.73(s)	.27(s)$^{(C)}$	.7(s)	.3(s)
CO_2	160(g)	27(g)		160(g)		160(g)		160(g)
H_2O	1(g)	.1(g)		1(g)		450(g)		450(g)
C	.2(g)	.02(g)	.196(s)	.004(s)$^{(C)}$	.15(s)	.05(s)$^{(C)}$	.14(s)	.06(s)$^{(C)}$
Approx. Total Stream	160$^{(A)}$	27	1	160$^{(A)}$	1$^{(B)}$	610$^{(A)}$	1$^{(B)}$	610$^{(A)}$

*Gaseous Effluent Stream

(A) Plus 250,000 SCFH of diluent air

(B) Plus soluble fluorides and water

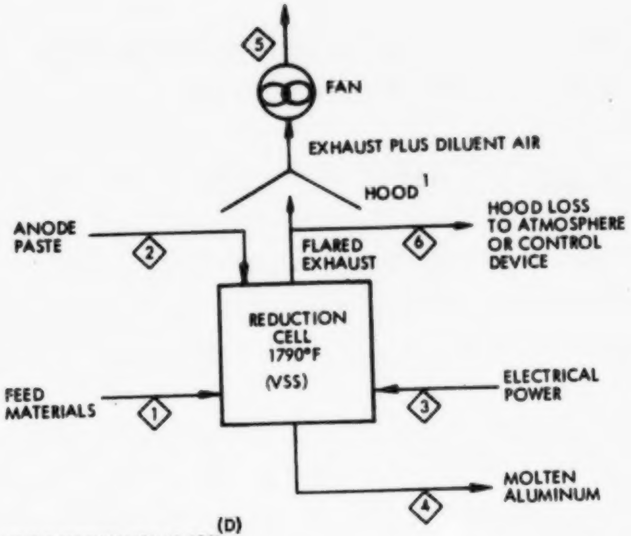
(C) Ref. 4208

Source	Calc. Fluoride Emission Factor - lb F/ton Al		
	Process A	Process B	Process C
Treated Hood Exhaust Emission	23.72	5.58	7.20
Untreated Hood Loss to Atmosphere	6.51	6.51	6.51
Total Emission to Atmosphere from Cell	30.23	12.09	13.71

Reported Average Overall Horizontal Stud Cell Soluble Fluoride Emission Factor = 10.12 lb F/ton Al$^{(C)}$. (Reflects the utilization of series abatement systems by a significant portion of the industry)

Figure 3-6. Electrolytic Aluminum Production -- Controlled Process Model, Horizontal Stud Soderberg Cell

B



5
FAN
EXHAUST PLUS DILUENT AIR
HOOD 1
ANODE PASTE
2
FLARED EXHAUST
6
HOOD LOSS TO ATMOSPHERE OR CONTROL DEVICE
REDUCTION CELL 1790°F (VSS)
FEED MATERIALS
1
ELECTRICAL POWER
3
MOLTEN ALUMINUM
4

1. HOOD EFFICIENCY IS 80%(D)

BASIS - 2070 LB ALUMINUM PRODUCED PER DAY PER VSS CELL

PROCESS STREAMS - LB/HR

Material	Stream Number					
	1	2	3	4	5*	6*
HF					1.54 (g)$^{(C,D)}$	.27 (g)
Na_3AlF_6	2.5 (s)$^{(B)}$				.13 (s)$^{(D)}$ as F	.13 (s) as F
AlF_3	3.3 (s)$^{(B)}$					
Total Fluorides$^{(E)}$	5.8				-	-
Total as F$^{(E)}$	3.6				1.59	.39
Alumina	165				1 (s)	.1 (s)
Anode Mat'l, as C		50				
Aluminum				86		
CO_2					150 (g)	37 (g)
H_2O					1 (g)	.1 (g)
C					.2 (g)	.02 (g)
Electrical Power			660 KWH			
Approx. Total Stream	170	50	--	86	150$^{(A)}$	37

*Gaseous effluent stream

(A) Plus 30,000 SCFH of diluent air

(B) Ref 4250

(C) Ref 4254

(D) Ref 4208

(E) The balance not shown is fluoride absorption by the cathode

Soluble F Evolution Factor = 46 lb F/ton aluminum produced.

Figure 3-7. Electrolytic Aluminum Production - Vertical Stud Soderberg Cell, Uncontrolled Process Model

capture efficienty (actual experience, Reference 4208). The balance of the fluoride not shown is absorbed in the cathode.

Fluoride Emission Control Techniques. Both solid and particulate soluble fluoride are evolved from the VSS cell during operation. Abatement techniques utilized for this process (which are identical to those used for the other alumina reduction processes) are presented as controlled process models in Figure 3-8. Typical usage is Process C.

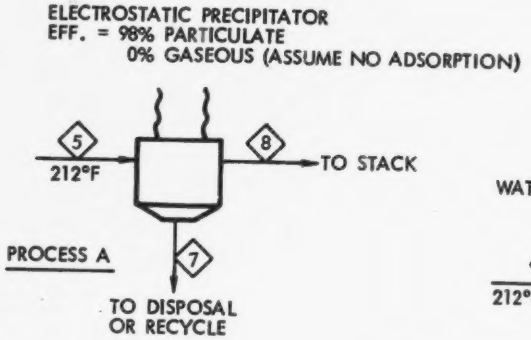
The VSS, because of the absence of channels, allows the use of a fume-collecting skirt around the base of the anode. The air volume required for fume collection is significantly lower than for the HSS. The resultant fume concentration is such that the CO and tar can be burned to reduce the tar content of the exhaust gas, oxidize the fume tars and prevent them from collecting in an fouling the ducting system. Maintenance of the skirts is a problem (melting, deformation) as is maintenance of the alumina crust to form an effective barrier to prevent evolution of fume from the pot into the rooms.

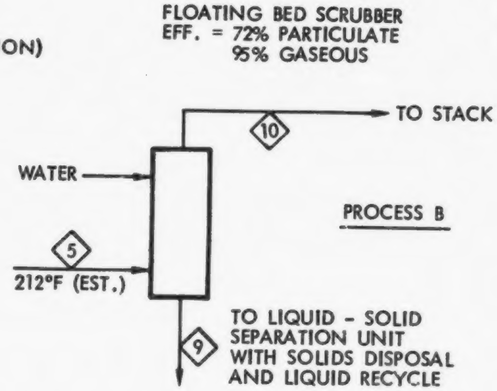
Fluoride Emissions. Soluble fluoride emission from the vertical stud Soderberg was 7.20 tons (as F) in 1970 (Reference 4208) or about 14% of the total from this industry. This corresponds to an average overall fluoride abatement efficiency of 79% (Reference 4208). The emission level will increase to 16,000 tons annually in the year 2000 if production projections are correct and if current control level is maintained. If 99% control is established, there will be 800 tons (as F) of fluoride emitted from this process in the year 2000.

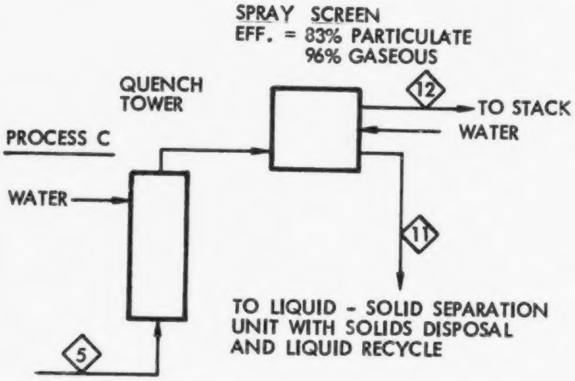
3.2.6 Economic Analysis

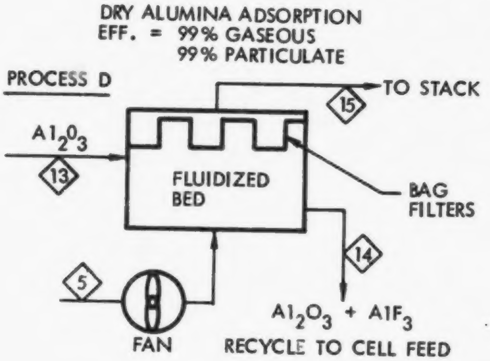
3.2.6.1 Basic Process

The estimated economics for the production of primary aluminum ingots by the prebaked anode process, without the costs imposed by fluoride emission control, are presented in Table 3-7. Process economics for vertical stud and horizontal stud Soderberg processes are similar, and the data of


ELECTROSTATIC PRECIPITATOR
EFF. = 98% PARTICULATE
0% GASEOUS (ASSUME NO ADSORPTION)
5
212°F
8
TO STACK
7
PROCESS A
TO DISPOSAL
OR RECYCLE


FLOATING BED SCRUBBER
EFF. = 72% PARTICULATE
95% GASEOUS
TO STACK
10
WATER
PROCESS B
5
212°F (EST.)
TO LIQUID - SOLID
SEPARATION UNIT
WITH SOLIDS DISPOSAL
AND LIQUID RECYCLE
9


SPRAY SCREEN
EFF. = 83% PARTICULATE
96% GASEOUS
QUENCH
TOWER
12
TO STACK
WATER
PROCESS C
WATER
11
TO LIQUID - SOLID SEPARATION
UNIT WITH SOLIDS DISPOSAL
AND LIQUID RECYCLE
5


DRY ALUMINA ADSORPTION
EFF. = 99% GASEOUS
99% PARTICULATE
PROCESS D
TO STACK
15
Al2O3
13
FLUIDIZED
BED
BAG
FILTERS
14
5
FAN
Al2O3 + AlF3
RECYCLE TO CELL FEED

Material	
	5
HF	1.
Na_3AlF_6	.
AlF_3	as
Total as F	1.
Alumina	1(
CO_2	150
H_2O	1(
C	.2
Approx. Total Stream	150

*Gaseous Effluent St

(A) Plus 30,000 SCFH

(B) Plus water and so

(C) Ref 4208

A

BASIS - 2070 LB ALUMINUM PRODUCED PER DAY VERTICAL STUD SODERBERG CELL

PROCESS STREAMS - LBS/HR

	Steam Number										
	5	6*	7	8*	9	10*	11	12*	13	14	15*
	1.54(g) .13(s) as F	.27(g) .13(s) as F	.127(s) as F	1.54(g) .003(s)$^{(C)}$ as F	.09(s) as F	.08(g)$^{(C)}$ .04(s)$^{(C)}$ as F	.11(s) as F	.06(g)$^{(C)}$ .02(s)$^{(C)}$ as F		1.58(s)$^{(C)}$ as F	.015(g)$^{(C)}$ .001(s)$^{(C)}$ as F
	1.59	.39	.13	1.47	.09	.11	.11	.08		1.58	.015
	1(s) 150(g) 1(g) .2(g)	.1(s) 37(g) .1(g) .02(g)	.98(s) .196(s)	.02(s)$^{(C)}$ 150(g) 1(g) .004(s)$^{(C)}$	.72(s) .15(s)	.28(s)$^{(C)}$ 150(g) 60(g)(Est) .05(s)$^{(C)}$	.83(s) .17(s)	.17(s)$^{(C)}$ 150(g) 60(g) .03(s)$^{(C)}$	20(s)(Est) .198(s)	21(s)(Est) .198(s)	.01(s)$^{(C)}$ 150(g) 1(g) .002(s)$^{(C)}$
al	150$^{(A)}$	17	1	150	1$^{(B)}$	210$^{(A)}$	1$^{(B)}$	210$^{(A)}$	20	21	150$^{(A)}$

luent Stream

,000 SCFH of diluent air.

er and soluble fluorides.

Source	Calc. Fluoride Emission Factor - lb F/ton Al			
	Process A	Process B	Process C	Process D
Treated Hood Exhaust Emission	34.19	2.56	1.86	0.35
Untreated Hood Loss to Atmosphere	9.07	9.07	9.07	9.07
Total Emission to Atmosphere from Cell	33.26	11.63	10.93	9.42

Reported Average Overall Vertical Stud Cell Soluble Fluoride Emission Factor = 9.66 lb F/ton Al$^{(C)}$
(Reflects the utilization of series abatement systems)

Figure 3-8. Electrolytic Aluminum Production -- Controlled Process Model, Vertical Stud Soderberg Cell

B

Table 3-7. Estimated Economics of Aluminum Production (Pollution Control Cost Excluded)

	Plant Capacity		
	60 M tons/yr	120 M tons/yr	250 M tons/yr
Total Capital Investment(1)	48 $MM	90 $MM	175 $MM
Production Costs			
Direct Costs			
Alumina(2) (1.9 tons Al_2O_3/Ton Al)	130.09 $/ton Al	130.09 $/ton Al	130.09 $/ton Al
Electrode Materials (Approx. 0.6 tons C/Ton Al)	26.40	26.40	26.40
Cryolite (0.05 Tons/Ton Al)	12.60	12.60	12.60
Aluminum Fluoride (0.03 Tons AlF_3/Ton Al)	10.05	10.05	10.05
Miscellaneous (Fluorspar, Soda Ash, etc.)	8.00	8.00	8.00
Electric Energy (16000 kwh/ton at 0.35 cents/kwh)	56.00	56.00	56.00
Labor (Operating, Maintenance, Supervision and Indirect)	60.00	52.60	45.00
TOTAL DIRECT COSTS	303.14	295.74	288.14
Indirect Cost			
Depreciation	80.00	75.00	70.00
Interest (at 7%, 20% debt)	11.20	10.50	9.80
Taxes and Insurance	20.00	18.50	17.00
Plant and Labor Overhead	20.00	18.00	15.00
TOTAL INDIRECT	131.20	122.00	111.80
Manufacturing Cost ($/ton Al)	434.34	417.74	399.94
General and Sales Expenses ($/ton Al)	8.69	8.35	8.00
f.o.b. Cost ($/ton Al)	443.03	426.09	407.94
Product Revenue ($/ton Al)	580.00	580.00	580.00
Profit After Taxes (at 50%) ($/ton Al)	68.49 $/ton Al	76.96 $/ton Al	86.03 $/ton Al
Cash Flow ($MM/yr)	8.9 $MM/yr	18.2 $MM/yr	39.0 $MM/yr
Return on Investment (ROI), %	10.7 %	12.8 %	17.0 %
Cost of Alumina (including shipping)			

(1) Costs of Prebake Anode Unit: Manufacturing Costs for Soderberg processes are similar.

Cost of alumina (including shipping)	$/Ton Al_2O_3
(2) Bauxite (5.00 $/Ton FOB mine at 2.5 tons bauxite/ton Al_2O_3 with an 18 $MM fixed investment)	12.50
Shipping (2.00 $/ton bauxite, Jamaica to Gulf Coast)	5.00
Bauxite to Alumina	
Direct costs	
Soda (0.25 tons/ton Al_2O_3)	8.50
Coal (0.25 tons/ton Al_2O_3)	2.00
Fuel Oil (0.125 tons/ton Al_2O_3)	2.88
Lime (0.0625 tons/ton Al_2O_3)	1.14
Operating labor	2.85
Supervision and Fringe Benefits	2.85
Maintenance and Supplies	2.25
Indirect Costs	
Depreciation	14.50
Taxes and Insurance	0.50
Plant and Labor Overhead	1.00
Shipping ($12.50/ton Al_2O_3, Gulf Coast to Pacific Northwest by rail)	12.50
Manufacturing Cost of Al_2O_3 ($/ton)	$68.47/ton

Table 3-7 is valid for these processes, prior to the addition of fluoride emission control systems. The model plant was assumed to be located in the Pacific Northwest to take advantage of the availability of inexpensive power*. In addition, the firm was assumed to own a bauxite mine in Jamaica and an alumina facility in the Gulf Coast area. The general process economic assumptions and bases for the economic analyses are those of Section 3.1.1, Economic Analysis - Discussion.

The uncontrolled aluminum process model has a mean estimated ROI of 13.0%.

3.2.6.2. Impact of Controls

The addition of emission control equipment causes a sharp decrease in ROI for all of the abatement processes except the dry adsorption process. ROI's after emission control range from 7.9 to 15.1%. The ΔROI's go from 2% to 26%. The ΔROI's versus plant capacity curves for each control process (as applied to the individual production processes) are almost completely flat (Figure 3-9 illustrates the ΔROI versus capacity curves for PBA control processes). A major part of the variation cited above arises from differences between the capital and operating costs of the different emission control processes. The emission control processes are generally unitized to cover a pot-line, so that plant capacity differences did not affect the per ton cost of control. Since the ΔROI curve is rather flat, both large and small primary aluminum producers should respond to similar added pollution control requirements in the same way. Because most aluminum plants have some existing pollution control facilities, the impact of added equipment to achieve possible new standards of control would not necessarily be as great as that shown in Figure 3-9 .

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*Bonneville Power Administration states that the actual 1970 billing rate was 1.7 mills per kwh ±0.3 mill per kwh for the aluminum facilities in the Pacific Northwest. In the analysis, 3.5 mills per kwh was used since an increase is expected in the next few years. In this case, 3.5 mills per kwh is conservative.

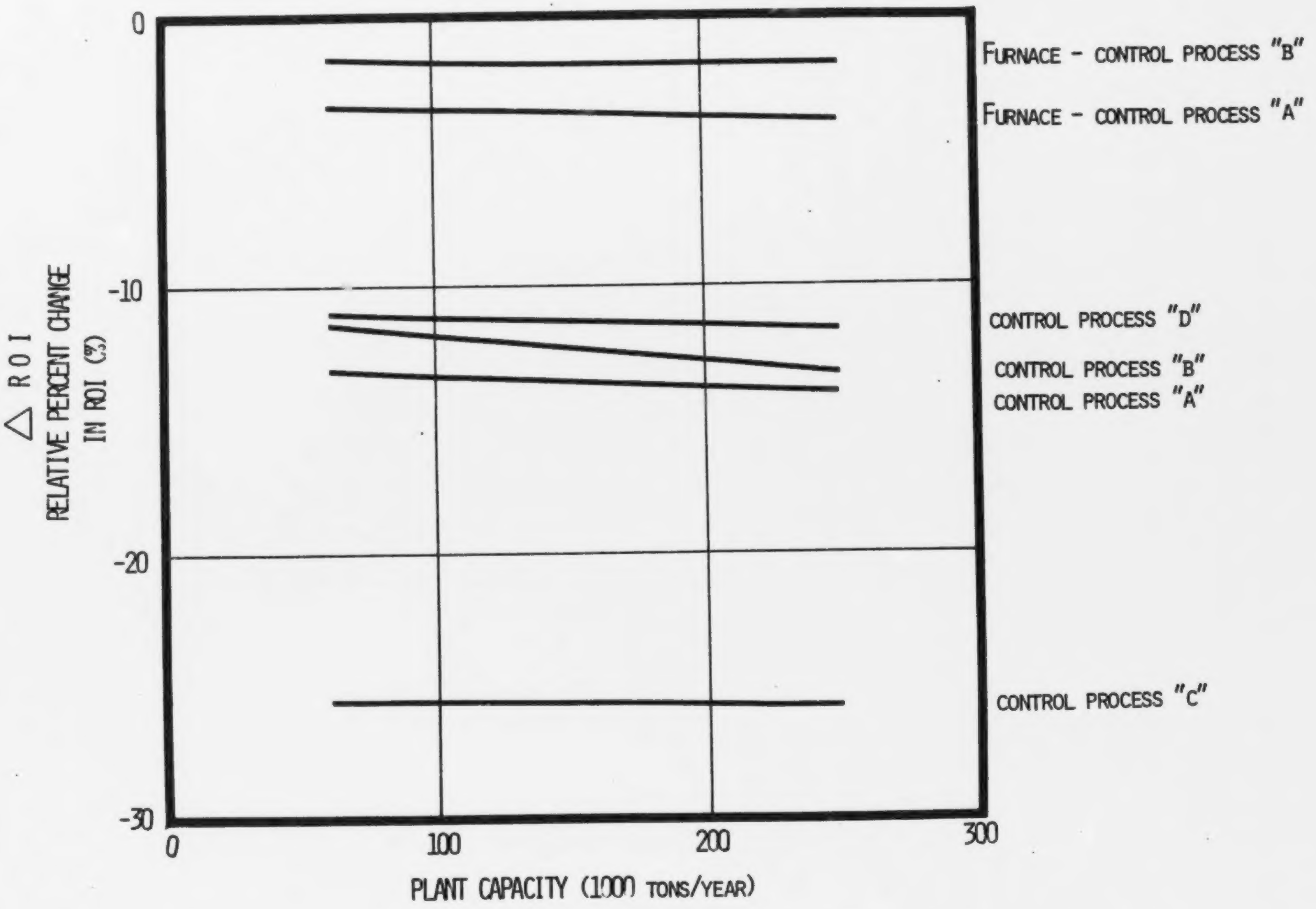


Figure 3-9. Effect of Pollution Control Cost on the Aluminum Industries Return on Investors' Equity - Prebaked Anode Process

Tables 3-8 through 3-21 present estimates of the economics of the various pollution control processes, as applied to each of the three primary production processes. The bases employed for the calculations, and the assumptions on which the estimates rest, are those contained in Section 3.1.1 under the heading "Control Cost Economics."

For all the fluoride emission control systems other than the dry alumina adsorption process, the vertical stud Soderberg enjoys an advantage in lowered control costs due to its relatively low diluent air requirements (about 15% of the diluent air stipulated for the PBA and HSS production units). The dry alumina adsorption process (currently proprietary to the Aluminum Company of America) has by far the lowest pollution control cost for the two production systems on which it may be used - $6.44/ton for the PBA process and $3.38/ton for the VSS process.

Table 3-21 summarizes control costs for the three production processes, the various control processes, and a "typical" 120,000 ton per year plant.

Table 3-8. Prebaked Anode Aluminum Production (4) - Estimated Economics of Control Process A
Basis - 8514 Tons Al Per Year Per Precipitator (one 25 cell pot line)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Floating Bed Scrubber, 2 at 12' diameter by 12' - 6", 8 ft/sec velocity, mass transfer coefficient of 80 mols/(hr) (ft^3) (atm), 2 in. W.G. pressure drop, 109,000 cfm, 46 horsepower, neoprene lined steel.	117 (6)	4391 4383 4392 4390	3.02		353
				Capital Subtotal		353
				Indirects (@ 15%)		53
				Contingency (@ 20%)		71
				Total Capital (as of January 1971)		477

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.24	0.25		0.49
Subtotal				0.49
Water (21)	(330 gpm, 90% recycle)			0.04
Disposal (22)				-
Total Operating Cost				0.53

Total Operating Cost ($/hr)	0.53
Taxes and Insurance (2%, 330 days)	1.20
Capital (7.1%, 330 working days)	4.28
Pollution Control Cost ($/hr)	6.01
Pollution Control Cost ($/ton)	5.59

Table 3-9. Prebaked Anode Aluminum Production(5) - Estimated Economics of Control Process B Basis - 8514 Tons Al Per Year Per 2 Scrubbers (one 25 cell pot line)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Quench Tower, 10' diameter by 30' height, neoprene lined steel	42	(a)	3.05		128
2	Spray Screen, 64 ft^2, 30 lb/hr loading, 5000 gpm, 46 horsepower energy requirement, fiberglass reinforced polyester	30	4383 4392	3.83		115
3	Liquid Solid Separation, 25 ft^2 30 lb/hr loading, 5000 gpm, 50,000 gal capacity, neoprene lined steel	18	4398 4392	4.22		76
	Capital Subtotal					319
	Indirects (@ 15%)					48
	Contingency (@ 20%)					64
	Total Capital (as of January 1971)					431

(a) Company private design information

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.04	0.20		0.24
2	0.24	0.32		0.56
3	0.10	0.06		0.16
Subtotal				0.96
Water(21) (5700 gpm, 90% recycle)				0.64
Disposal(22)				-
Total Operating Cost				1.60

Total Operating Cost ($/hr)	1.60
Taxes and Insurance (2%, 330 days)	1.09
Capital (7.1%, 330 working days)	3.86
Pollution Control Cost ($/hr)	6.55
Pollution Control Cost ($/ton)	15.19

Table 3-10. Prebaked Anode Aluminum Production(8) - Estimated Economics of Control Process C
Basis - 3406 Tons Al Per Year Per Process (one 10 cell pot line)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1.	Electrostatic Precipitator, 109,000 cfm, 0.9 in W.G pressure drop.	240	(a)	1.69		406
	Capital Subtotal					406
	Indirects (@ 15%)					61
	Contingency (@ 20%)					81
	Total Capital (as of January 1971)					548

(a) SEE FOOTNOTE 20.

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.46	0.38		0.84
Subtotal				0.84
Water(21)				-
Disposal(22)				-
Total Operating Cost				0.84

Total Operating Cost ($/hr)	0.84
Taxes and Insurance (2%, 330 days)	1.38
Capital (7.1%, 330 working days)	4.91
Pollution Control Cost ($/hr)	7.13
Pollution Control Cost ($/ton)	6.63

Table 3-11. Prebaked Anode Aluminum Production(11) - Estimated Economics of Control Process D
Basis - 50,000 Tons Al Per Year Per System

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Dry alumina adsorption system.		4254			2,000.
					Capital Subtotal	2,000.
					Indirects (@ 15%)	(a)
					Contingency (@ 20%)	400.
					Total Capital (as of January 1971)	2,400.

(a) Included in Installed Cost, Reference 4254

(b) See Reference 4254

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	(a)	(a)		13.07
Subtotal				13.07
Water(21)				-
Disposal(22)				-
Total Operating Cost				13.07

Total Operating Cost ($/hr)	13.07
Taxes and Insurance (2%, 330 days)	6.06
Capital (7.1%, 330 working days)	21.52
Pollution Control Cost ($/hr)	40.65
Pollution Control Cost ($/ton)	6.44

Table 3-12. Prebaked Anode Baking Furnace(14) - Estimated Economics of Control Process A Basis - 50,000 Ton Al Per Year Plant

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Electrostatic Precipitator, 147,000 cfm 0.9 in W.G. pressure drop, power requirement 120 horsepower, monel clad.	324	(a)	1.69		548
	Capital Subtotal					548
	Indirects (@ 15%)					82
	Contingency (@ 20%)					110
	Total Capital (as of January 1971)					740

(a) See Footnote (20)

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.63	0.38		1.01
Subtotal				1.01
Water(21)				-
Disposal(22)				-
Total Operating Cost				1.01

Total Operating Cost ($/hr)	1.01
Taxes and Insurance (2%, 330 days)	1.87
Capital (7.1%, 330 working days)	6.63
Pollution Control Cost ($/hr)	9.51
Pollution Control Cost ($/ton)	1.51

Table 3-13. Prebaked Anode Baking Furnace(14) -- Estimated Economics of Control Process B

Basis - 50,000 Ton Al Per Year Plant

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Spray Tower, 2 at 10' diameter by 30', 8 ft/sec velocity, 76,000 cfm, 5 grains/sec loading, 2 in W.G. pressure drop, required power 73 horsepower, neoprene lined steel.	91	4383 4391 4392	2.44		222
				Capital Subtotal		222
				Indirects (@ 15%)		33
				Contingency (@ 20%)		44
				Total Capital (as of January 1971)		299

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.38	0.25		0.63
Subtotal				0.63
Water(21) (3340 gpm, 90% recycle)				0.40
Disposal(22)				-
Total Operating Cost				1.03

Total Operating Cost ($/hr)	1.03
Taxes and Insurance (2%, 330 days)	0.75
Capital (7.1%, 330 working days)	2.68
Pollution Control Cost ($/hr)	4.46
Pollution Control Cost ($/ton)	0.69

Table 3-14. Horizontal Stud Soderberg Aluminum Production(4) - Estimated Economics of Control Process A Basis - 8514 Tons Al Per Year Per Precipitator (one 25 cell pot line)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Electrostatic Precipitator, 146,000 cfm, 0.9 in W.G. pressure drop.	324	(a)	1.69		548
					Capital Subtotal	548
					Indirects (@15%)	82
					Contingency (@20%)	110
					Total Capital (as of January 1971)	740

(a) See Footnote 20.

All control economics footnotes are located in Section 3.1.1pages 3-10 and 3-11.

Operating Cost ($ /hr.)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.62	0.51		1.13
Subtotal				1.13
Water(21)				–
Disposal(22)				–
Total Operating Cost				1.13

Total Operating Cost ($/hr)	1.13
Taxes and Insurance (2%, 330 days)	1.87
Capital (7.1%, 330 working days)	6.63
Pollution Control Cost ($/hr)	9.63
Pollution Control Cost ($/ton)	8.96

Table 3-15. Horizontal Stud Soderberg Aluminum Production(5) - Estimated Economics of Control Process B Basis - 8514 Tons Al Per Year Per 2 Scrubbers (one 25 cell pot line)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Floating Bed Scrubber, 2 at 8' diameter by 16' - 8", 8 ft/sec velocity, mass transfer coefficient of 80 mols/(hr)(ft^3)(atm), 2 in. W.G. pressure drop.	139	4391 4383 4392 4390	3.02		420
				Capital Subtotal		420
				Indirects (@ 15%)		63
				Contingency (@ 20%)		84
				Total Capital (as of January 1971)		567

Operating Cost ($ /hr.)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.29	0.30		0.59
Subtotal				0.59
Water(21) (440 gpm, 90% recycle)				0.05
Disposal(22)				-
Total Operating Cost				0.64

Total Operating Cost ($/hr)	0.64
Taxes and Insurance (2%, 330 days)	1.43
Capital (7.1%, 330 working days)	5.08
Pollution Control Cost ($/hr)	7.15
Pollution Control Cost ($/ton)	6.65

All control economics footnotes are located in Section 3.1.1pages 3-10 and 3-11.

Table 3-16. Horizontal Stud Soderberg Aluminum Production(9) -- Estimated Economics of Control Process

Basis - 5110 Tons Al Per Year Per Tower (one 15 cell pot line)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Spray Tower, 12' diameter by 28' 4 in W.G. pressure drop, fan at 75% efficiency, 87,500 cfm, 74 horsepower power requirement, neoprene lined steel.	80(10)	4383 4391 4392 4387	3.44		275
				Capital Subtotal		275
				Indirects (@ 15%)		41
				Contingency (@ 20%)		55
				Total Capital (as of January 1971)		371

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.39	0.25		0.64
Subtotal				0.64
Water(21)	(800 gpm, 90% recycle)			0.10
Disposal(22)				-
Total Operating Cost				0.74

Total Operating Cost ($/hr)	0.74
Taxes and Insurance (2%, 330 days)	0.94
Capital (7.1%, 330 working days)	3.33
Pollution Control Cost ($/hr)	5.01
Pollution Control Cost ($/ton)	7.73

Table 3-17. Vertical Stud Soderberg Aluminum Production - Estimated Economics of Control Process A Basis - 60,000 Tons Al Per Year Per Precipitator (one 176 cell pot line)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Electrostatic Precipitator, 108,000 cfm, 0.9 in W.G. pressure drop.	230	(a)	1.69		389
				Capital Subtotal		389
				Indirects (@ 15%)		58
				Contingency (@ 20%)		78
				Total Capital (as of January 1971)		525

(a) See Footnote 20.

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11.

Operating Cost ($ /hr.)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.46	0.38		0.84
Subtotal				0.84
Water(21)				-
Disposal(22)				-
Total Operating Cost				0.84

Total Operating Cost ($/hr)	0.84
Taxes and Insurance (2%, 330 days)	1.33
Capital (7.1%, 330 working days)	4.71
Pollution Control Cost ($/hr)	6.88
Pollution Control Cost ($/ton)	0.91

Table 3-18. Vertical Stud Soderberg Aluminum Production - Estimated Economics of Control Process B
Basis - 60,000 Tons Al Per Year Per Scrubber (one 176 cell pot line)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Floating Bed Scrubber, 2 at 12' diameter by 12' - 6", 8 ft/sec velocity, mass transfer coefficient of 80 mols/(hr)(ft^3)(atm), 2 in. W.G. pressure drop, 108,000 cfm, 45 horsepower, neoprene lined steel	116	4391 4383 4392 4390	3.02		350
					Capital Subtotal	350
					Indirects (@ 15%)	53
					Contingency (20%)	70
					Total Capital (as of January 1971)	473

All control economics footnotes are located in Section 3.1.1pages 3-10 and 3-11.

Operating Cost ($ /hr.)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.24	0.25		0.49
Subtotal				0.49
Water(21) (330 gpm, 90% recycle)				0.04
Disposal(22)				-
Total Operating Cost				0.53

Total Operating Cost ($/hr)	0.53
Taxes and Insurance (2%, 330 days)	1.19
Capital (7.1%, 330 working days)	4.24
Pollution Control Cost ($/hr)	5.95
Pollution Control Cost ($/ton)	0.79

Table 3-19. Vertical Stud Soderberg Aluminum Production - Estimated Economics of Control Process C Basis - 23,800 Tons Al Per Year Per Process (one 70 cell pot line)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Quench Tower, 10' diameter by 30' height, neoprene lined steel	42	(a)	3.05		128
2	Spray Screen, 64 ft^2, 30 lb/hr loading - 5000 gpm, 46 horsepower, fiberglass reinforced polyester	30	4383 4392	3.83		115
3	Liquid solid separation, 25 ft^2, 30 lb/hr loading, 5000 gpm, 50,000 gal capacity, neoprene lined steel	18	4398 4392	4.22		76
	Capital Subtotal					319
	Indirects (@ 15%)					48
	Contingency (@20%)					64
	Total Capital (as of January 1971)					431

(a) Company private design information.

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Operating Cost ($ /hr.)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.04	0.20		0.24
2	0.24	0.32		0.56
3	0.10	0.06		0.16
Subtotal				0.96
Water[21] (5700 gpm, 90% recycle)				0.64
Disposal[22]				-
Total Operating Cost				1.60

Total Operating Cost ($/hr)	1.60
Taxes and Insurance (2%, 330 days)	1.09
Capital (7.1%, 330 working days)	3.86
Pollution Control Cost ($/hr)	6.55
Pollution Control Cost ($/ton)	2.18

Table 3-20. Vertical Stud Soderberg Aluminum Production - Estimated Economics of Control Process D Basis - 50,000 Ton Al Per Year Per System

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Dry alumina adsorption system		4254			600
	Capital Subtotal					600
	Indirects (@ 15%)					(a)
	Contingency (@20%)					120
	Total Capital (as of January 1971)					720

(a) Included in Installed Costs, Reference 4254
(b) See Reference 4254

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	(b)	(b)		13.07
Subtotal				13.07
Water$^{(21)}$				-
Disposal$^{(22)}$				-
Total Operating Cost				13.07

Total Operating Cost ($/hr)	13.07
Taxes and Insurance (2%, 330 days)	1.82
Capital (7.1%, 330 working days)	6.45
Pollution Control Cost ($/hr)	21.34
Pollution Control Cost ($/ton)	3.38

Table 3-21. Cost of Emission Control - Typical 120,000 ton/year Plant

Control Process* / Production Process	A		B		C		D	
	$/Ton	ΔROI %	$/Ton	ΔROI %	$/Ton	ΔROI %	$/Ton	ΔROI %
PBA	6.63	13	5.59	12	15.19	25	6.44	11
PBA Furnace	1.51	3	0.75	2	-	-	-	-
HSS	8.96	18	6.65	14	7.73	15	-	-
VSS	0.91	2	0.79	2	2.18	4	3.38	4

(*As identified on the Controlled Process Models for each production process - Figures 3-3 , 3-4 , 3-6 , and 3-8)

3.3 IRON AND STEEL INDUSTRY

3.3.1 General

The iron and steel industry incorporates a wide variety of fluoride emitting processes producing products which range from pelletized iron ore to cast, forged and welded high alloy steel shapes. This report covers only those primary high temperature metal production processes which are now, or are projected to be, major sources of fluoride evolution and emission. The many plants of the industry contain almost every possible combination of these process elements, making generalization on an industry wide basis extremely difficult.

The fluorides evolved and emitted by the industry are gaseous hydrogen fluoride and solid particulate calcium fluoride.

3.3.2 Industry Description

The primary high temperature iron and steel process elements which are current major sources of fluoride evolution and emission are:

(1) Iron ore pelletizing
(2) Iron ore sintering
(3) Blast furnace operation
(4) Open hearth furnace operation
(5) Electric arc furnace operation
(6) Basic oxygen furnace operation

Iron ore pelletizing operations occur almost exclusively at the mine sites; iron ore sintering is almost always performed at a plant site in conjunction with blast furnace operations. The remaining process elements, listed by location in Appendix 7-2, occur in every possible combination, singly and in multiple, with and without blast furnace operations. A specimen integrated iron and steel plant sinters iron ore to aggregate the fines; charges the sintered iron ore, coke, and limestone into a blast furnace to reduce the iron ore to pig iron; and then converts the pig iron to steel, using a protective molten flux (limestone and fluorspar) cover, steel scrap and alloy additives in one or more of the three steel producing processes (the open hearth, electric arc, and basic oxygen furnaces).

In each case, wherever the high temperature process involves a source of hydrogen (water or fuel), gaseous hydrogen fluoride is evolved and emitted, accompanied by solid calcium fluoride particulate dispersed in the exit gas stream. Where no source of hydrogen is available, calcium fluoride is evolved and emitted as dispersoid particulate. On the basis of thermochemical equilibria calculations, other fluoride species are not evolved or emitted to any measurable extent.

Because of the variety of processes and diversity of process element combinations at the various plant locations, detailed descriptions are provided under the individual process description sections which follow; the reader is referred to Schueneman, High and Bye(4055) and Varga and Lownie(4225) for a more exhaustive treatment.

3.3.3 Production Trends

During the past decade the U.S. steel industry has been undergoing a multifaceted transition as a result of technological change. Evolutionary improvements of both practice and equipment have been made to gain more efficient production.

Beneficiation of iron ore leading to the development of pelletized ore was a major development of the American steel industry in the period following World War II. The result of this effort was that in 1968, of some 130 million tons of ore consumed in iron making, more than 100 million tons was agglomerated, and consumption of pellets had increased to about 50 million tons.(4286,4287) This development has contributed to a reduction in coke consumption and to an increase in the output of pig iron for existing blast furnace facilities. The evolution of cryogenic technology, permitting the low-cost production of oxygen in quantity, led to the development of oxygen-supplemented steelmaking practice and culminated in the acceptance of the basic oxygen process (BOF).

The BOF produced 48 million tons in 1968 at 90% of rated installed capacity; this level is expected to almost double by 1975, to over 80 million tons, requiring investment of about $800 million. Production of steel from electric furnaces will grow at a similar rate in this period from 16 million to about 28 million tons. The balance of the steel requirements will be met by open hearth production, which will decline from 60 million tons in 1968 to about 30 million tons in 1975.(4285,4287) Hot metal requirements are expected to rise only gradually; the decline of open hearth production coupled with the increased yield from continuous casting and the dramatic increase in BOF production will satisfy the projected hot metal needs. Thus, no increase of blast furnace capacity beyond the current estimated 100 million tons will be required before 1975, although older and smaller units may be modernized or even replaced with more efficient plants.(4286,4287) Existing coke oven capacity will also be adequate, although it too is being modernized. A summary of the current and estimated production through the year 2000 is presented in Table 3-22.

The integrated steel plant will continue to be the predominant type of manufacturing facility. Current nominal production levels for integrated steel plants are more than 1 million tons/year while plants currently being designed or installed have planned production levels on the order of 2 to 3 million tons per year. This size of steel production facility will be used for new plant design at least through the next decade.(4286,4287)

3.3.4 Fluoride Control and Emissions Summary

The only reported attempt to control soluble fluoride emissions in the iron and steel industry is from a program pursued at the U.S. Steel works in Geneva, Utah.(4179) High fluoride iron ore (about 3000 ppm) was used in the process, and the local fluoride levels in the area were such that damage suits were brought against the company.

Table 3-22. Steel Production

Process	1968 Million Tons	1975 Million Tons	Estimated Growth Rate	Extrapolated(1) to Year 2000 Million Tons
Blast Furnace (Ore Tonnage)	130	120	0%	120
Sintering (Ore Tonnage)	50	35	-4.7%	To a constant value of 13(1)
Pelletizing (Ore Tonnage)	50	65	~4.7%(1)	To a constant level of 107(1)
Open Hearth	66	30	-12%	To zero level
Basic Oxygen	48	80	7.6%	To a constant value of ~135
Electric Arc	16	28	8.3%	To a constant value of ~35
Total Steel Production	130	138	0.85%	170

(1) No reference data - TRW estimate.

The abatement procedure adopted by U. S. Steel involved inclusion of limestone in the feed material to the sintering operation. This reportedly reduced fluoride emissions by 50%. Further treatment of the gas stream with finely ground calcium hydroxide gave further reductions in fluoride content. Particulate matter was collected in electrostatic precipitators.

The off-gases from the open hearth furnaces were also treated with calcium hydroxide for fluoride adsorption. Particulates were removed using cyclone separators and electrostatic precipitators in series. This approach is of particular interest since the conversion of gaseous to particulate fluoride material will result in fluoride control at the same time particulates are controlled. The iron and steel industry has done much more work on control of particulates than on control of fluorides.

It cannot be considered that the optimal solution to a fluoride abatement problem in Utah necessarily constitutes a general solution. In particular, the shortage of water in that area might preclude potential scrubber approaches. Other collection and transfer equipment currently employed in the majority of the industry is aimed specifically at collecting and transporting the economically recoverable dusts -- the ore, iron and other metal oxides, and metallic iron -- and other airborne particulate material that forms visible effluent plumes.

The individual pollution abatement systems for the process elements are discussed under the individual process element headings.

Unfortunately, almost no definitive information has been published on fluoride evolution and emission from the iron and steel industry in the U.S., with the exception of that small part of the industry using high fluoride ore. An account of a fluoride emission reduction program at a facility in Utah has been reported as cited above(4179) and several publications have been presented for European sources. None of the published data has distinguished between soluble fluorides and CaF_2 emission.

Fluorides enter the iron and steel making process as a minor component in iron ore (concentrations range as high as 3000 ppm) and as fluorspar for use in fluxing. The fluoride in the iron ore is partially volatilized at the temperatures involved where sintering or nodulizing of the blast furnace feed material is practiced.(4179,4055) Otherwise, the volatilization occurs in the blast furnace. In the latter case, the evolved fluoride tends to be captured (adsorbed) by the limestone that constitutes a portion of the blast furnace charge and is collected or emitted as a particulate rather than a gas. The usage of fluorspar in the iron and steel industry and steel production for various furnace types, as reported by the Bureau of Mines, can be combined to yield average fluoride input values of 1.74, 6.14, and 3.63 pound fluoride/ton steel for open hearth, BOF, and electric furnaces, respectively.

Estimates of the fluoride emissions from the iron and steel industry vary widely as shown by comparing the following items of information:

(1) Singmaster and Breyer(4297) report an emission total for steelmaking furnaces (basic oxygen, open hearth, and electric) of 1716 tons of fluorides (soluble and insoluble) per year for 1969.

(2) Sinter plant emissions have been reported(4385) as varying from 0.3 to 5.7 parts per million at two eastern plants, with 150 parts per million reported from western plants (4385) prior to the institution of lime abatement processes.

(3) The total fluoride emission factors attributed to the AISI in the report by Environmental Engineering Inc.-Herrick Associates(4385) are as follows:

Furnace	Reported Total Fluoride Emission, lb/NT Wet Collection	Dry Collection
Open Hearth	0.002	0.030
Basic Oxygen	0.002	0.030
Electric Arc	0.004	0.009

(4) TRW-RRI experience indicates an emission factor typical of an Eastern open hearth plant of 0.185 pound/NT steel in terms of soluble fluoride.

(5) According to the Annual Report of the British Alkali and Works Chief Inspectors,(4276) approximately 50% of the input fluoride to open hearth plants is evolved.

In view of the wide variations in the few reported values, the failure to distinguish between soluble and insoluble fluorides, and the lack of correlation with ore fluoride analysis, TRW performed thermochemical analyses to determine the equilibria fluoride species and concentration values for the high temperature reactions occurring in each of the integrated iron and steel plant primary processes. For the varying process conditions, the thermochemical equilibrium analyses indicated from 12 to 99.3% evolution of feed fluorides as gaseous HF if a hydrogen source was present in the feed charge (including fuel and combustion air) and evolution of CaF_2 as the only measurable species if no hydrogen source was available in the high temperature process. The identification of the theoretical proportions of HF and CaF_2 in the effluent streams on the basis of hydrogen availability and reaction zone temperatures is very significant. CaF_2 has low environmental impact, and can be removed as a particulate by the control devices normally employed by the industry. Detailed results of these equilibria analyses are given in the following sections under the appropriate process headings.

The equilibria analyses together with the following assumptions were used to define the species emitted and the soluble fluoride emission factors:

(1) Based on Reference (4276), about 50% of the input fluorides exit in the slag. Therefore, gaseous fluorides emitted from uncontrolled iron and steel processes are estimated at 50% of the theoretical equilibrium analyses values computed for the high temperature zones. The mechanisms involved in this reduction are probably adsorption and chemisorption of gaseous fluorides on solid particles, particularly limestone.

(2) The weighted average fluoride content of iron ore was estimated assuming (on the basis of the geographical distribution of industry capacity) 95% usage of normal fluoride content ores at 650 parts per million F concentration*, and 5% usage of high fluoride content ores at 3000 parts per million F concentration.

---

*Iron ore was assumed to contain the same average fluoride content as the earth's crust(4242).

(3) The distribution of wet and dry control systems cited from Reference (4225) in each of the control process model diagrams was used in conjunction with the control system efficiencies presented in the diagrams for the calculations.

Table 3-23 presents the resulting evolution and emission factors and tonnages for the processes and the industry. Mass balances and schematics for each of the processes are presented under the individual process headings. It should be noted that the estimated open hearth emission factor is much higher than the reference (4385) values. It was assumed that there are no process hydrogen sources in the BOF and electric arc steel making systems; therefore, soluble fluoride evolution from these processes was estimated as zero.

The estimated soluble fluoride evolution for the iron and steel industry was 69,100 tons for 1968, with an emission of 64,600 tons of soluble fluorides during that year. In 2000, soluble fluoride evolution for the industry is projected to be 49,800 tons; soluble fluorides emitted if current practices continue would be 46,400 tons. If control processes capable of 99% abatement efficiency are adapted, soluble fluoride emission by the industry would drop to 500 tons in the year 2000.

3.3.5 Process Description and Economics

3.3.5.1 Iron Ore Sintering and Pelletizing

With very few exceptions, modern blast furnaces use as charge iron ore which has been agglomerated by sintering or pelletizing, or sized by screening. As noted earlier, pelletizing plants are generally located at the mine site. Sintering plants are normally a portion of an integrated iron and steel operation. The trend towards a straight pellet or pellet-sinter practice will continue in essentially 100% of industry practice. Since both sintering and pelletizing involve high temperature agglomeration of fluoride-containing material, the processes are quite similar. Therefore,

Table 3-23. Soluble Fluoride Evolution and Emission From the Iron and Steel Industry

	Iron Ore Sintering	Iron Ore Pelletizing	Blast Furnace	Basic Open Hearth Furnace	Basic Oxygen Furnace	Electric Arc Furnace	Total Iron and Steel Industry
1968 Production (10^6 tons product/year)	50(A) 53(B)	50(A) 53(B)	130(A) 87(B)	66	48	16	130(E)
2000 Production (10^6 tons product/year)	13(A) 14(B)	107(A) 113(B)	120(A) 80(B)	0	135	35	170(E)
Soluble fluoride evolution factor(D) (lb F/ton product)	.73	.73(C)	.088	.81	0(F)	0(F)	1.06(E)
Soluble fluoride emission factor(D) (lb F/ton product)	.69	.69(C)	.065	.77	0	0	0.99(E)
1968 soluble fluoride evolution (10^3 tons F/year)	19.3	19.3	3.8	26.7			69.1
2000 soluble fluoride evolution (10^3 tons F/year)	5.1	41.2	3.5	0	0	0	49.8
1968 soluble fluoride emission (10^3 tons F/year)	18.2	18.2	2.8	25.4	0	0	64.6
2000 soluble fluoride emission with current technology (10^3 tons F/year)	4.8	39.0	2.6	0	0	0	46.4
2000 soluble fluoride emission with 99% control technology (10^3 tons F/year)	.05	.4	.04	0	0	0	.5

Notes:
(A) Expressed as ore tonnage in process feed.
(B) Expressed as product tonnage.
(C) TRW estimation.
(D) Reflects estimated 5% usage of high fluoride content (3000 ppm) ore, 95% usage of average fluoride content (650 ppm) ore and application of wet control processes as noted on the control mass balances.
(E) Expressed as per ton of steel production.
(F) Based on assumption that there are no process hydrogen sources in the BOF and electric arc furnaces.

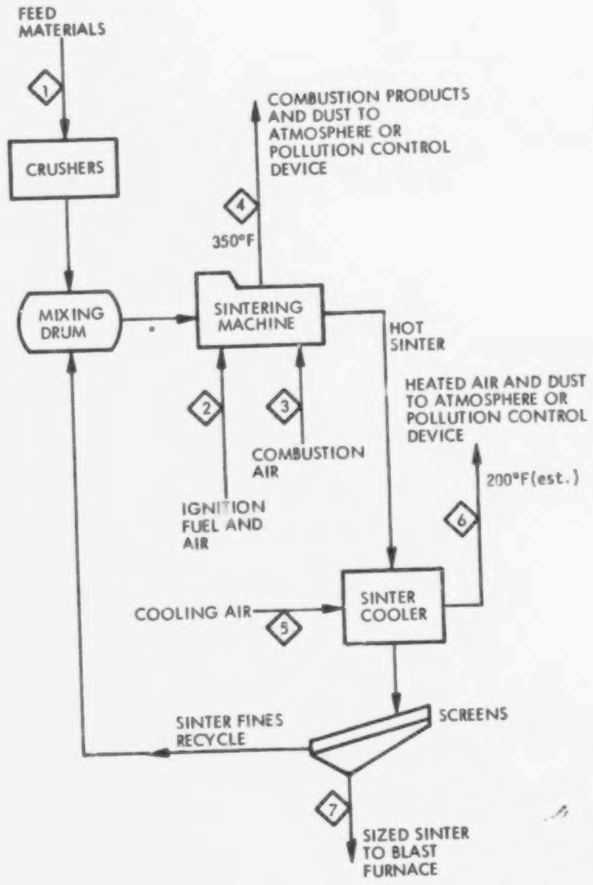
only sintering will be considered in detail and the assumption is made that sintering and pelletizing are essentially interchangeable from a fluoride evolution standpoint.

Process Description. Figures 3-10 and 3-11 present flow diagrams and mass balances for normal and high fluoride content iron ore sintering operations. Modern sinter plants range from 2000 to about 10,000 tons per day.

Present and Future Production Levels. The program for the development of beneficiation and agglomeration techniques to enhance the quality of ore charged to blast furnaces has culminated in the treatment of ores previously considered of too low a grade to be used in the furnaces. The first pelletizing plant was installed in 1949. By the end of 1968, U. S. pelletizing capacity totaled some 50 million tons (more than 35% of the 130 million tons charged to blast furnaces) and several million tons of additional capacity was being installed.(4286,4287) The growth rate of the pelletizing process is expected to be about 4.7% annually to a constant level of about 107 million tons of ore pelletized per year through 2000.

The increase in pelletizing will be accompanied by a decrease in the ore sintering process from a level of 50 million tons in 1968 to a constant level of approximately 13 million tons annually in the year 2000.

Future trends in ore treatment will include eventual use of prereduced agglomerates, pellets, or briquettes which will permit the furnace operator to vary capacity to satisfy the varying hot metal demands without blowing in additional furnaces (prereduced pellets could increase capacity by at least 50%). In addition, research can also be expected on the possibility of an integrated charge, i.e., agglomerates containing all ingredients - carbon, iron units, and flux (probably precalcined). Finally, attention will be focused on the use of computers to calculate burdens charged to the blast furnace.(4286, 4287)


FEED MATERIALS
1
CRUSHERS
MIXING DRUM
SINTERING MACHINE
COMBUSTION PRODUCTS AND DUST TO ATMOSPHERE OR POLLUTION CONTROL DEVICE
4
350°F
2
3
IGNITION FUEL AND AIR
COMBUSTION AIR
HOT SINTER
HEATED AIR AND DUST TO ATMOSPHERE OR POLLUTION CONTROL DEVICE
200°F(est.)
6
COOLING AIR
5
SINTER COOLER
SCREENS
SINTER FINES RECYCLE
7
SIZED SINTER TO BLAST FURNACE

BASIS - 2000 TONS/DAY OF SINTER PRODUCED

PROCESS STREAMS - TONS/DAY

Material	Stream Number						
	1	2	3	4*	5	6*	7
HF				0.77(g)			
CaF_2 equiv.	3.05			$0.02(s)^{(A,B,D)}$		$0.34(s)^{(A,B)}$	$1.16(s)^{(A,B,C,E)}$
Total Fluorides	3.05			0.79		0.34	1.16
Total as F	1.48			0.74		0.17	0.56
Iron Ore**	1900			19(s)		21(s)	
$\text{Limestone}^{(A,B)}$	110						
Coke	500						
Water	40			250(g)			
Natural Gas		16					
Air (50% R.H.)		400	16000		2000	2000(g)	
N_2				12500(g)			
O_2				2000(g)			
CO				1000(g)			
CO_2				900(g)			
Sintered Ore							2000
Approx. Total Stream	2500	400	16000	16700	2000	2000	2000

*Gaseous Effluent Stream

(A) Reference 4179

(B) Reference 4053

(C) Reference 4055

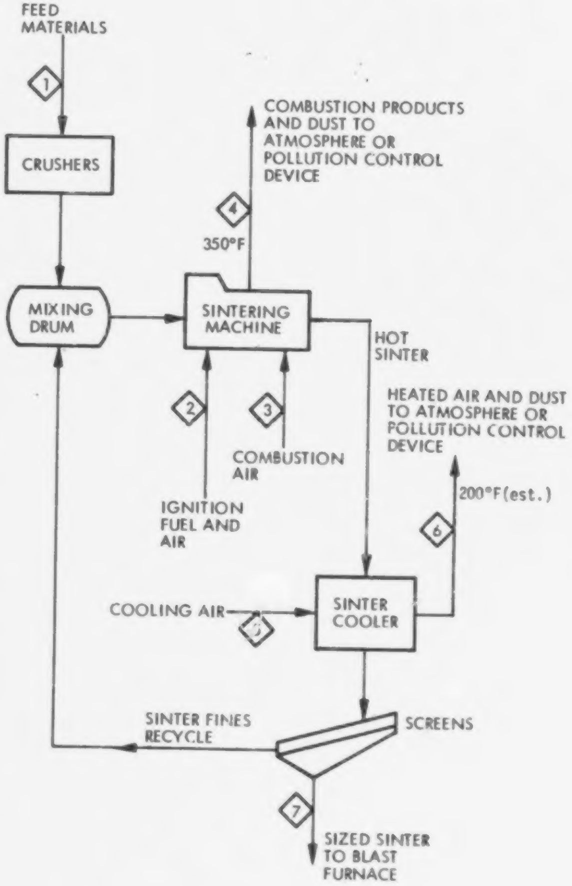
(D) Reference 4249

(E) Does not include CaF_2 added from control device recycle streams.

Soluble Fluoride Evolution Factor = 0.73 lbF/ton Sinter

NOTE: Fluoride content of the iron ore reflects 95% usage of 650 ppm fluoride content ore and 5% usage of 3000 ppm fluoride content ore.

Figure 3-10. Iron Ore Sintering - Uncontrolled Process Model


FEED MATERIALS
1
CRUSHERS
MIXING DRUM
SINTERING MACHINE
COMBUSTION PRODUCTS AND DUST TO ATMOSPHERE OR POLLUTION CONTROL DEVICE
4
350°F
HOT SINTER
2
3
IGNITION FUEL AND AIR
COMBUSTION AIR
HEATED AIR AND DUST TO ATMOSPHERE OR POLLUTION CONTROL DEVICE
200°F(est.)
6
COOLING AIR
5
SINTER COOLER
SINTER FINES RECYCLE
SCREENS
7
SIZED SINTER TO BLAST FURNACE

BASIS - 2000 TONS/DAY OF SINTER PRODUCED

PROCESS STREAMS - TONS/DAY

Material	Stream Number						
	1	2	3	4*	5	6*	7
HF				3.01(g)			
CaF_2 equiv.	11.9			0.09(s)$^{(A,B,D)}$		1.35(s)$^{(A,B)}$	4.55(s)$^{(A,B,C,E)}$
Total Fluorides	11.9			3.10		1.35	4.55
Total as F	5.8			2.90		0.68	2.22
Iron Ore**	1900			19(s)		21(s)	
Limestone$^{(A,B)}$	110						
Coke	500						
Water	40			250(g)			
Natural Gas		16					
Air (50% R.H.)		400	16000		2000	2000(g)	
N_2				12500(g)			
O_2				2000(g)			
CO				1000(g)			
CO_2				900(g)			
Sintered Ore							2000
Approx. Total Stream	2500	400	16000	16700	2000	2000	2000

*Gaseous Effluent Stream

**Fluorine Content of Ore = 0.3 wt.%.

(A) Reference 4179

(B) Reference 4053

(C) Reference 4055

(D) Reference 4249

(E) Does not include CaF_2 added from control device recycle streams

Soluble fluoride evolution factor of facilities utilizing high fluoride content (3000 ppm) iron ore = 2.86 lbF/ton of sinter produced.

Figure 3-11. High Fluoride Content Iron Ore Sintering - Uncontrolled Process Model

Fluoride Emission Control Techniques. The emission control techniques employed currently in conjunction with normal and high fluoride content iron ore are presented in Figures 3-12 and 3-13. As noted in Figure 3-12, Processes A and B are used in over 90% of the sinter plants.

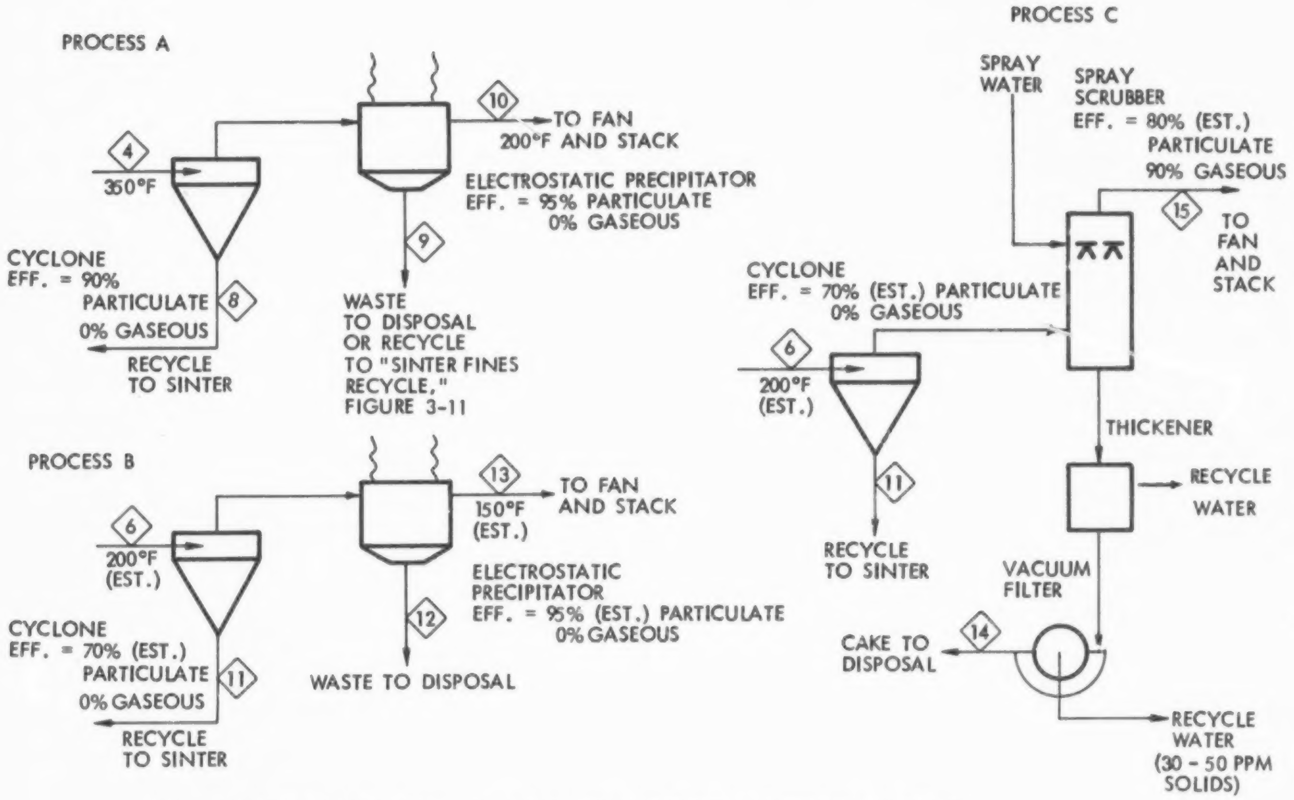
Ore sinter plants are hooded for collection and transport of dust at the majority of particulate discharge points in the system. The ore sintering machine is hooded to vent, under induced draft, the dust-laden waste combustion gas to the dust collectors shown.

Fluoride Emissions. Estimated soluble fluoride emissions from sintering and pelletizing of iron ore were each 18,200 tons in 1968. By 2000, production will have decreased for iron sintering to where soluble fluoride emissions, using currently employed control techniques, are estimated at 4800 tons. For pelletizing, production increases could cause the soluble fluorides emitted to rise to 39,000 tons by 2000, if currently employed control techniques were used. If control techniques capable of 99% efficiency are employed, soluble fluoride emissions in 2000 would drop to 50 tons for sintering and 400 tons for pelletizing.

3.3.5.2 Blast Furnace Operations

Pig iron is produced by high temperature reduction of the iron ore charged to the blast furnace. Other portions of the blast furnace burden include coke and limestone; natural gas and air are injected to furnish part of the heat. The high temperature environment, coupled with the availability of hydrogen from the combustion products, causes volatilization of much of the CaF_2 present in the ore feed and conversion of a portion of the volatilized fluorides to HF.

Process Description. Figures 3-14 and 3-15 present flow diagrams and mass balances for production of pig iron from normal and high fluoride ores by the use of the blast furnace.

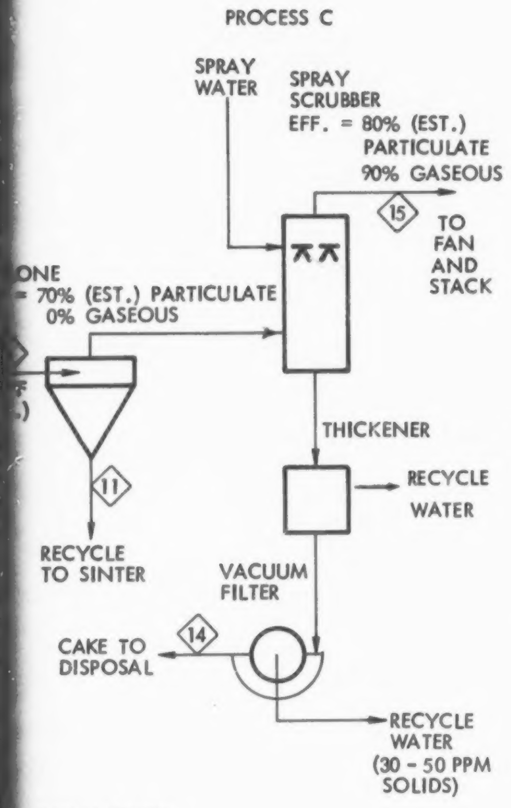

PROCESS A
4
350°F
CYCLONE
EFF. = 90%
PARTICULATE
0% GASEOUS
8
RECYCLE TO SINTER
10
TO FAN AND STACK
200°F
ELECTROSTATIC PRECIPITATOR
EFF. = 95% PARTICULATE
0% GASEOUS
9
WASTE TO DISPOSAL OR RECYCLE TO "SINTER FINES RECYCLE," FIGURE 3-11
PROCESS B
6
200°F (EST.)
CYCLONE
EFF. = 70% (EST.)
PARTICULATE
0% GASEOUS
11
RECYCLE TO SINTER
13
TO FAN AND STACK
150°F (EST.)
ELECTROSTATIC PRECIPITATOR
EFF. = 95% (EST.) PARTICULATE
0% GASEOUS
12
WASTE TO DISPOSAL
PROCESS C
SPRAY WATER
SPRAY SCRUBBER
EFF. = 80% (EST.)
PARTICULATE
90% GASEOUS
15
TO FAN AND STACK
CYCLONE
EFF. = 70% (EST.) PARTICULATE
0% GASEOUS
6
200°F (EST.)
11
RECYCLE TO SINTER
THICKENER
RECYCLE WATER
VACUUM FILTER
14
CAKE TO DISPOSAL
RECYCLE WATER (30 - 50 PPM SOLIDS)

NOTE: PROCESS A FOR TREATMENT OF EVOLVED GASES FROM SINTERING MACHINE
PROCESSES B AND C FOR TREATMENT OF EVOLVED GASES FROM SINTERING COOLER
ASSUMES NO ADSORPTION OF FLUORIDES ON PARTICULATE MATTER.

Ma
HF
CaF_2
Total
Total
Iron
Water
Air (
N_2
O_2
CO
CO_2
Appro St

* G
Over
(A)
(B)
(C)

A


PROCESS C
SPRAY WATER
SPRAY SCRUBBER
EFF. = 80% (EST.) PARTICULATE
90% GASEOUS
15
TO FAN AND STACK
ONE
= 70% (EST.) PARTICULATE
0% GASEOUS
.)
THICKENER
11
RECYCLE WATER
RECYCLE TO SINTER
VACUUM FILTER
14
CAKE TO DISPOSAL
RECYCLE WATER
(30 - 50 PPM SOLIDS)

ERING MACHINE
OM SINTERING COOLER
MATTER.

BASIS - 2000 TONS/DAY OF SINTER PRODUCED

PROCESS STREAMS - TONS/DAY

Material	Stream Number						
	4	6	8	9	10*	11	
HF CaF_2 equiv.	0.77(g) 0.02(s)	 0.34(s)	 0.02(s)$^{(C)}$	 0.002(s)$^{(C)}$	0.77(g) 0.0003(s)(Est)	 0.24(s)(Est)	 0.
Total Fluorides Total as F	0.79 0.74	0.34 0.17	0.02 0.01	0.002 0.001	0.77 0.73	0.24 0.12	0. 0.
Iron Ore Water Air (50% R.H.) N_2 O_2 CO CO_2	19(s) 250(g) 12500(g) 2000(g) 1000(g) 900(g)	21(s) 10000(g)	17$^{(C)}$	1.9$^{(C)}$	0.1(s) 250(g) 10000(g) 12500(g) 2000(g) 1000(g) 900(g)	14.7(s)(Est)	6
Approx. Total Stream	16700	10000	18	2	16700	15	6

Source	Soluble Fluoride Emissi	
	Process A	Pr
Sinter Machine	0.73	
Sinter Cooler	–	
Assumed Fugitive	0	
Total Soluble Fluoride Emission Factor	0.73	

* Gaseous Effluent Stream

Overall process soluble fluoride emission factor = 0.69 lb F/ton sinter(A)

(A) Reflects estimated 5% usage of high fluoride (3000 ppm) content ore, 95% usage of averag of wet control processes to 6.5% (Reference 4225) of the sintering facilities.

(B) Reference 4006

(C) Reference 4055

B

BASIS - 2000 TONS/DAY OF SINTER PRODUCED

PROCESS STREAMS - TONS/DAY

Stream Number									
4	6	8	9	10*	11	12	13*	14	15*
0.77(g) 0.02(s)	0.34(s)	0.02(s)(C)	0.002(s)(C)	0.77(g) 0.0003(s)(Est)	0.24(s)(Est)	0.10(s)(Est)	0.005(s)(Est)	0.08(s)(B)	0.02(s)(Est)
0.79 0.74	0.34 0.17	0.02 0.01	0.002 0.001	0.77 0.73	0.24 0.12	0.10 0.05	0.005 0.003	0.08 0.04	0.02 0.01
19(s) 250(g) 12500(g) 2000(g) 1000(g) 900(g)	21(s) 10000(g)	17(C)	1.9(C)	0.1(s) 250(g) 10000(g) 12500(g) 2000(g) 1000(g) 900(g)	14.7(s)(Est)	6.0(s)(Est)	0.3(s) 10000(g)	5.0(s)(B)	1.3(s) 10000(g)
16700	10000	18	2	16700	15	6	10000	5	10000

Source	Soluble Fluoride Emission Factor - lb F/ton sinter		
	Process A	Process B	Process C
Sinter Machine	0.73	–	–
Sinter Cooler	–	–	–
Assumed Fugitive	0	0	0
Total Soluble Fluoride Emission Factor	0.73	0	0

nt Stream

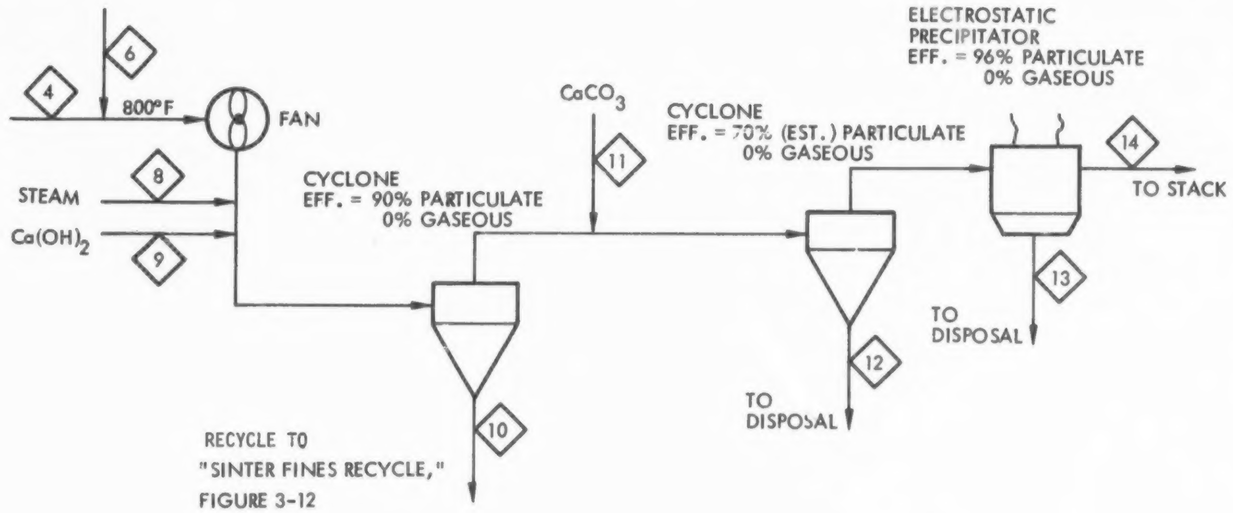
soluble fluoride emission factor = 0.69 lb F/ton sinter(A)

timated 5% usage of high fluoride (3000 ppm) content ore, 95% usage of average fluoride content (650 ppm) ore and application rol processes to 6.5% (Reference 4225) of the sintering facilities.

006

055

Figure 3-12. Iron Ore Sintering - Controlled Process Model


4
6
800°F
FAN
STEAM
8
$Ca(OH)_2$
9
CYCLONE
EFF. = 90% PARTICULATE
0% GASEOUS
$CaCO_3$
11
10
RECYCLE TO
"SINTER FINES RECYCLE,"
FIGURE 3-12
CYCLONE
EFF. = 70% (EST.) PARTICULATE
0% GASEOUS
12
TO
DISPOSAL
ELECTROSTATIC
PRECIPITATOR
EFF. = 96% PARTICULATE
0% GASEOUS
14
TO STACK
13
TO
DISPOSAL

A

BASIS - 2000 TONS/DAY OF SINTER PRODUCED
PROCESS STREAMS - TONS/DAY

Materials	Stream Number								
	4	6	8	9	10	11	12	13	14*
HF	3.01(g)								0.10(g)
CaF_2 equiv.	0.09(s)	1.35(s)			4.9(s)$^{(B)}$		1.48(s)(Est)	0.61(s)$^{(B)}$	0.03(s)(Est)
Total Fluorides	3.10	1.35			4.91		1.48	0.61	0.13
Total as F	2.90	0.68			2.40		0.72	0.30	0.12
Iron Ore	19(s)	21(s)			36$^{(B)}$		2.8(Est)	1.1$^{(B)}$	0.1(s)
Water	250(g)		4000$^{(B)}$						4250(g)
Air (50% RH)		10000(g)							10000(g)
N_2	12500(g)								12500(g)
O_2	2000(g)								2000(g)
CO	1000(g)								1000(g)
CO_2	900(g)								900(g)
$Ca(OH)_2$				14.4$^{(B)}$	13.5				
$CaCO_3$						46$^{(B)}$	32	12	1.0(s)
Approx. Total Stream	16700	10000	4000$^{(A)}$	14	54	46	35	13	30700

* Gaseous effluent stream

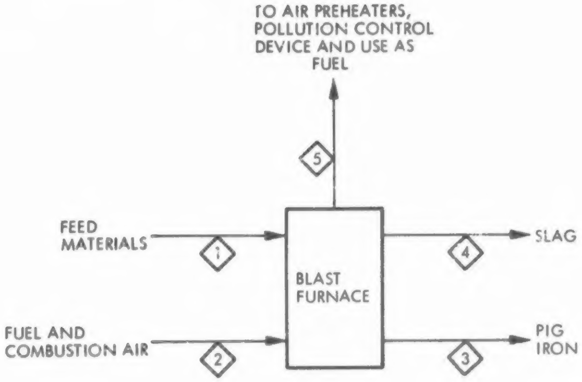
(A) Stream

Soluble fluoride emission factor of facilities utilizing high fluoride content (3000 ppm) iron ore = 0.095 lb F/Ton of Sinter Produced

(B) References 4055 and 4246

B

Figure 3-13. High Fluoride Content Iron Ore Sintering - Controlled Process Model


TO AIR PREHEATERS, POLLUTION CONTROL DEVICE AND USE AS FUEL
5
FEED MATERIALS
1
FUEL AND COMBUSTION AIR
2
BLAST FURNACE
4
SLAG
3
PIG IRON

BASIS - DAILY FURNACE PRODUCTION OF 1000 TONS OF PIG IRON

PROCESS STREAMS - TONS/DAY

Materials	Stream Number				
	1	2	3	4	5*
HF					0.046(g)
CaF_2	1.5 (s)		0	0.77(s)$^{(C,D)}$	0.67 (s)
Total Fluorides	1.5		0	0.77	0.71
Total as F	0.74		0	0.37	0.37
Sintered Iron Ore$^{(A)}$	1150				
Screened Iron Ore$^{(B)}$	400				
Coke	500				
$CaCO_3$ (Limestone)	60				
Natural Gas		20			
Air (50% R.H.)		2150			
Slag				230	
Pig Iron			1000		
H_2O					70(g)
N_2					1600(g)
H_2					130(g)
CO					1000(g)
CO_2					400(g)
Fe_2O_3					25(s)$^{(C)}$
Approx. Total Stream	2100	2200	1000	230	3300

* Gaseous effluent stream

(A) Contains 0.9 tons of CaF_2

(B) Contains 0.6 tons of CaF_2 equiv.

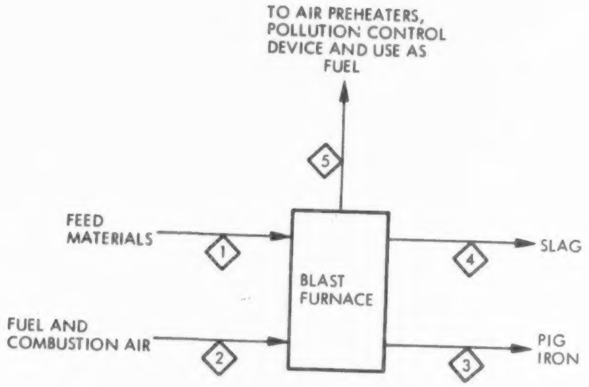
(C) Reference 4006

(D) Reference 4179

Soluable fluoride evolution factor = 0.088 lb F/ton pig iron

Note: Fluoride content of the iron ore and sinter reflects 95% usage of 650 ppm fluoride content ore and 5% usage of 3000 ppm fluoride content ore.

Figure 3-14. Pig Iron Production - Uncontrolled Process Model


TO AIR PREHEATERS, POLLUTION CONTROL DEVICE AND USE AS FUEL
5
FEED MATERIALS
1
FUEL AND COMBUSTION AIR
2
BLAST FURNACE
4
SLAG
3
PIG IRON

BASIS - DAILY FURNACE PRODUCTION OF 1000 TONS OF PIG IRON

PROCESS STREAMS - TONS/DAY

Materials	Stream Number				
	1	2	3	4	5*
HF					0.18(g)
CaF_2	6.0(s)		0	3.0 (s)$^{(C,D)}$	2.60(s)
Total Fluorides	6.0		0	3.0	2.78
Total as F	2.9		0	1.46	1.44
Sintered Iron Ore$^{(A)}$	1150				
Screened Iron Ore$^{(B)}$	400				
Coke	500				
$CaCO_3$ (Limestone)	60				
Natural Gas		20			
Air (50% R.H.)		2150			
Slag				230	
Pig Iron			1000		
H_2O					70(g)
N_2					1600(g)
H_2					130(g)
CO					1000(g)
CO_2					400(g)
Fe_2O_3					25(s)$^{(C)}$
Approx. Total Stream	2100	2200	1000	230	3300

* Gaseous effluent stream

(A) Contains 3.0 tons of CaF_2

(B) Contains 2.4 tons of CaF_2 equiv.

(C) Reference 4006

(D) Reference 4179

Soluble fluoride evolution factor of facilities utilizing high fluoride content (3000 ppm) iron ore = 0.34 lb F/ton pig iron

Figure 3-15. Pig Iron Production From High Fluoride Content Iron Ore - Uncontrolled Process Model

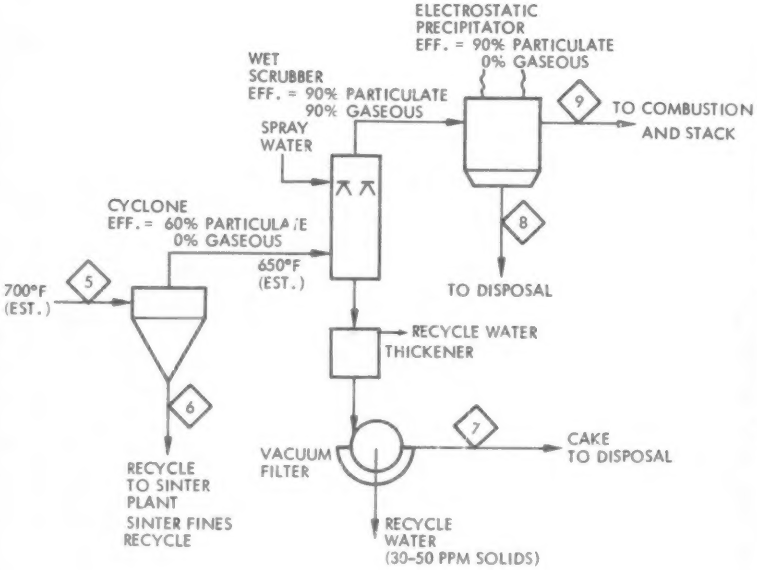
Present and Future Production Levels. Currently, pig iron is produced at the locations shown in Appendix 7.2. As noted earlier, the industry practice will shift to pellet or pellet-sinter feed completely. In 1968, the U.S. steel industry utilized 130 million tons of ore, both treated and untreated, in blast furnace burdens. The total amount of pellets charged to the blast furnaces for pig iron production was 50.7 million tons. The total amount of sinter product was 49.8 million tons, down from 51.6 million tons in 1967 and 54.7 million tons in 1966.

It is expected that the amount of ore tonnage consumed in blast furnace burdens will decrease slightly between now and the year 2000 to a level of about 120 million tons annually. This is because of expected higher furnace efficiencies and greater use of reusable scrap for hot metal.

Fluoride Emission Control Techniques. Flow diagrams and mass balances for the current method employed for fluoride control on normal and high fluoride content ores are presented in Figures 3-16 and 3-17.

Fluoride Emissions. Much of the gaseous HF evolved in the high temperature reduction zones is adsorbed in the upper, cooler zones of the burden or on the heavy load of particulate suspensoid carried by the blast furnace effluent gases. The portion of the cooled HF adsorbed on the particulate suspensoid is removed along with the dust in the dust control equipment. The remainder of the cooled gaseous HF is emitted when the blast furnace product gas is burned for energy recovery, or flared. Additional fluoride emission occurs when the pressure spikes developed as the result of "slips" (dropping charge breaks) are released to the atmosphere by the collection system "bleeders" (over-pressure relief valves).

Soluble fluoride emissions from blast furnace operations were 2800 tons during 1968, and will drop to 2600 tons in 2000 if current control practices are continued. If controls effective at the 99% level are adopted, soluble fluoride would drop to 40 tons.


ELECTROSTATIC PRECIPITATOR EFF. = 90% PARTICULATE 0% GASEOUS
WET SCRUBBER EFF. = 90% PARTICULATE 90% GASEOUS
SPRAY WATER
9
TO COMBUSTION AND STACK
CYCLONE EFF. = 60% PARTICULATE 0% GASEOUS
8
5
700°F (EST.)
650°F (EST.)
TO DISPOSAL
RECYCLE WATER
THICKENER
6
7
VACUUM FILTER
CAKE TO DISPOSAL
RECYCLE TO SINTER PLANT
SINTER FINES RECYCLE
RECYCLE WATER (30-50 PPM SOLIDS)

BASIS - DAILY FURNACE PRODUCTION OF 1000 TONS OF PIG IRON

PROCESS STREAMS - TONS/DAY

Material	Stream Number				
	5	6	7	8	9*
HF	0.046(g)		0.041		0.0046
CaF_2 equiv.	0.67 (s)	0.40(s)$^{(B)}$	0.24 (s)$^{(B)}$	0.024(s)$^{(B)}$	0.0026
Total Fluorides	0.71	0.40	0.28	0.024	0.007
Total as F	0.37	0.19	0.16	0.012	0.006
H_2O	70(g)				70(g)
N_2	1600(g)				1600(g)
H_2	130(g)				130(g)
CO	1000(g)				1000(g)
CO_2	400(g)				400(g)
Fe_2O_3	25(s)	15(s)$^{(B)}$	9(s)$^{(B)}$	9(s)$^{(B)}$	0.1(s)
Approx. Total Stream	3300	17	10	9	3300

Source	Soluble Fluoride Emission Factor - lb.F/ton Pig Iron
Blast Furnace	0.0087
Assumed Fugitive	0
Total Soluble Fluoride Emission Factor	0.0087

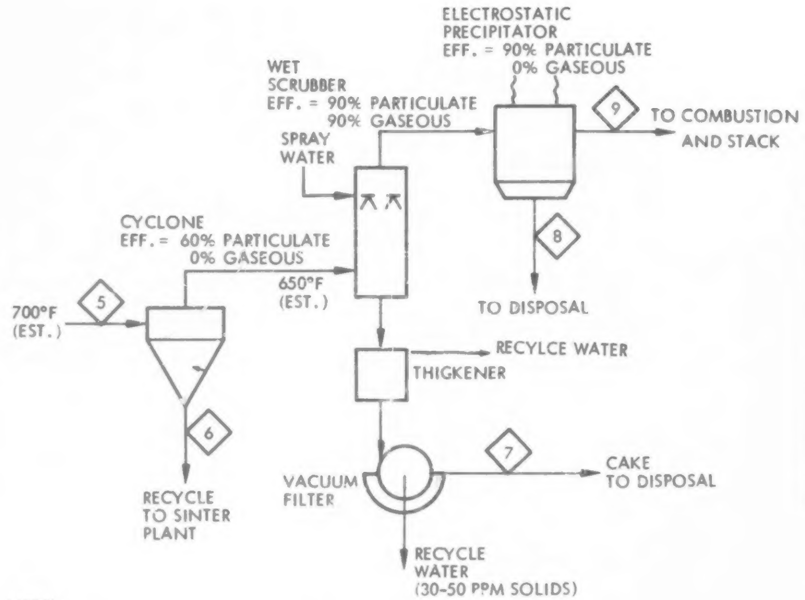
*Gaseous Effluent Stream

Overall process soluble fluoride emission factor = 0.055 lb.F/ton pig iron$^{(A)}$

(A) Reflects estimated 5% usage of high fluoride (3000 ppm) content ore, 95% usage of average fluoride content (650 ppm) ore and application of wet control processes to 30% (Reference 4225) of the blast furnace facilities.

(B) Reference 4055

Figure 3-16. Pig Iron Production - Controlled Process Model


ELECTROSTATIC
PRECIPITATOR
EFF. = 90% PARTICULATE
0% GASEOUS
WET
SCRUBBER
EFF. = 90% PARTICULATE
90% GASEOUS
SPRAY
WATER
9
TO COMBUSTION
AND STACK
CYCLONE
EFF. = 60% PARTICULATE
0% GASEOUS
8
650°F
(EST.)
700°F
(EST.)
5
TO DISPOSAL
RECYLCE WATER
THIGKENER
6
7
VACUUM
FILTER
CAKE
TO DISPOSAL
RECYCLE
TO SINTER
PLANT
RECYCLE
WATER
(30-50 PPM SOLIDS)

NOTE:
ASSUMES NO ADSORPTION OF FLUORIDES ON PARTICULATE MATTER.

BASIS - DAILY FURNACE PRODUCTION OF 1000 TONS OF PIG IRON

PROCESS STREAMS - TONS/DAY

Material	Stream Number				
	5	6	7	8	9*
HF	0.18(g)		0.16		0.018(g)
CaF_2 equiv.	2.60(s)	1.56(s)$^{(A)}$	0.94(s)$^{(A)}$	0.094(s)$^{(A)}$	0.010(s)
Total Fluorides	2.78	1.56	1.10	0.094	0.028
Total as F	1.44	0.76	0.61	0.046	0.022
H_2O	70(g)				70(g)
N_2	1600(g)				1600(g)
H_2	130(g)				130(g)
CO	1000(g)				1000(g)
CO_2	400(g)				400(g)
Fe_2O_3	25(s)	15(s)$^{(A)}$	9(s)$^{(A)}$	9(s)$^{(A)}$	0.1(s)
Approx. Total Stream	3300	17	10	9	3300

* Gaseous Effluent Stream

Soluble fluoride emission factor of facilities utilizing high fluoride content (3000 ppm) iron ore = 0.034 lb.F/ton pig iron

(A) Reference 4055

Figure 3-17. Pig Iron Production From High Fluoride Content Iron Ore - Controlled Process Model

3.3.5.3 Open Hearth Furnace Operations

Open hearth steelmaking in the U.S. dates back to 1870 and is currently declining in importance as the basic oxygen furnace process increases in capacity. The open hearth is actually a shallow hearth inside a rectangular furnace. The furnace charge, composed of molten pig iron ("hot metal"), scrap and flux, is heated by mixtures of natural gas, tar, and oil. High temperature oxidation of the carbon, silicon and manganese contained in the hot metal converts the charge to steel. The flux forms a slag with the oxidized silicon and manganese, and with portions of the sulfur and phosphorus impurities. The oxygen necessary for the oxidation comes, in the older furnaces, from the air and iron oxide portions of the charge; in the newer furnaces, this is supplemented with gaseous oxygen introduced through a water-cooled cover.

The flux employed is limestone, with fluorspar added. The fluorspar serves as the source for the majority of the fluorides evolved from the molten charge. Half of the evolved fluorides are converted to gaseous hydrogen fluoride and emitted from the furnace.

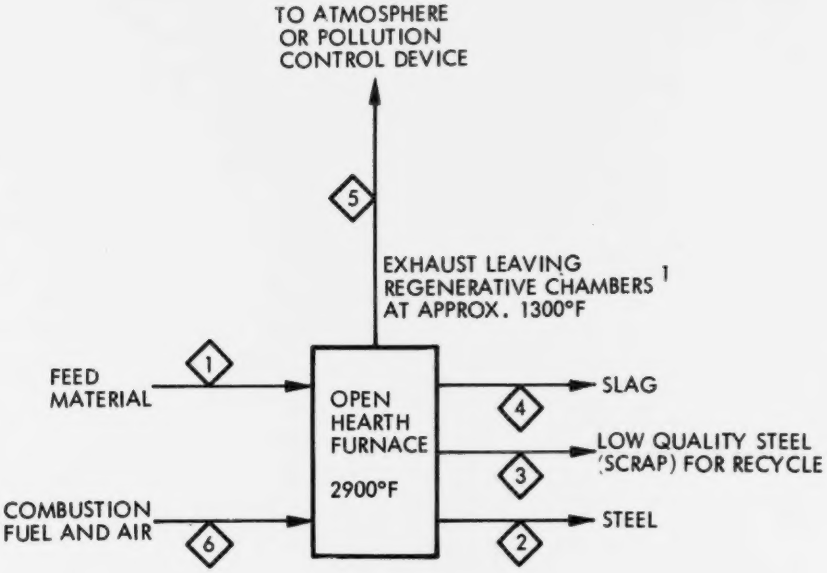
Process Description. Figures 3-18 and 3-19 present the process models and mass balances for the manufacture of steel (using both normal and high fluoride content iron ore) via the open hearth process without oxygen sources.

Production Trends. Open hearth operations accounted for 90% of steel production in the period after World War II. Open hearth output peaked at 105 million tons in 1955, and declined to 66 million tons in 1968 and about 60 million tons in 1969.(4286,4287) It is estimated that open hearth production will decline at a rate of about 12% annually to a near zero level, and will remain at that level through the year 2000.

Fluoride Emission Control Techniques. Figures 3-20 through 3-22 present process models and mass balances for the processes currently employed for control of emissions from open hearth operations. Normally, the covered open hearth furnaces are vented through checkerwork regenerators before passing the gases on to the waste heat boilers and dust abatement

BASIS - FURNACE
(2 HEAT

NON-OXYGEN LANCED


TO ATMOSPHERE
OR POLLUTION
CONTROL DEVICE
5
EXHAUST LEAVING
REGENERATIVE CHAMBERS 1
AT APPROX. 1300°F
FEED
MATERIAL
1
OPEN
HEARTH
FURNACE
2900°F
4
SLAG
LOW QUALITY STEEL
(SCRAP) FOR RECYCLE
3
COMBUSTION
FUEL AND AIR
6
STEEL
2

NOTE: (1) IF A WASTE HEAT BOILER IS INSTALLED, THE TEMPERATURE OF THE GASES LEAVING THIS UNIT WOULD BE ABOUT 500°F.

Material	
HF	
CaF_2	0.26
Total Fluorides	0.26
Total as F	0.13
Pig Iron (Hot)	100
Scrap	70
Iron Ore(A)	15
$CaCO_3$ (Limestone)	15
Raw Steel	
Low Quality Steel for Recycle	
Slag	
N_2	
O_2	
H_2O	
CO_2	
SO_2	
Fe_2O_3	
Air (50% R.H.)	
Fuel Oil	
Approx. Total Stream	200

* Gaseous effluent stream

(A) Contains 0.02 tons o

(B) Reference 4006

(C) Reference 889

Soluble fluoride evolutio

Note: Fluoride content o

content ore and 5% usage o

A

AVING
VE CHAMBERS 1
1300°F
SLAG
4
LOW QUALITY STEEL
(SCRAP) FOR RECYCLE
3
STEEL
2
URE
HIS
0°F.

BASIS - FURNACE CAPACITY OF 200 TONS/HEAT - NON OXYGEN LANCED
(2 HEATS PER DAY @ APPROX. 10 HOURS PER HEAT)

PROCESS STREAMS - TONS/HEAT

Material	Stream Number					
	1	2	3	4	5*	6
HF					0.066(g)	
CaF_2	0.26(s)$^{(B)}$			0.13 (s)$^{(C)}$		
Total Fluorides	0.26			0.13	0.066	
Total as F	0.13			0.063	0.063	
Pig Iron (Hot)	100					
Scrap	70					
Iron Ore$^{(A)}$	15					
$CaCO_3$ (Limestone)	15					
Raw Steel		155				
Low Quality Steel for Recycle			5			
Slag				18		
N_2					180(g)	
O_2					5(g)	
H_2O					12(g)	
CO_2					75(g)	
SO_2					0.3(g)	
Fe_2O_3					1(s)$^{(B)}$	
Air (50% R.H.)						235
Fuel Oil						15
Approx. Total Stream	200	155	5	18	270	250

* Gaseous effluent stream

(A) Contains 0.02 tons of CaF_2 equivalent

(B) Reference 4006

(C) Reference 889

B

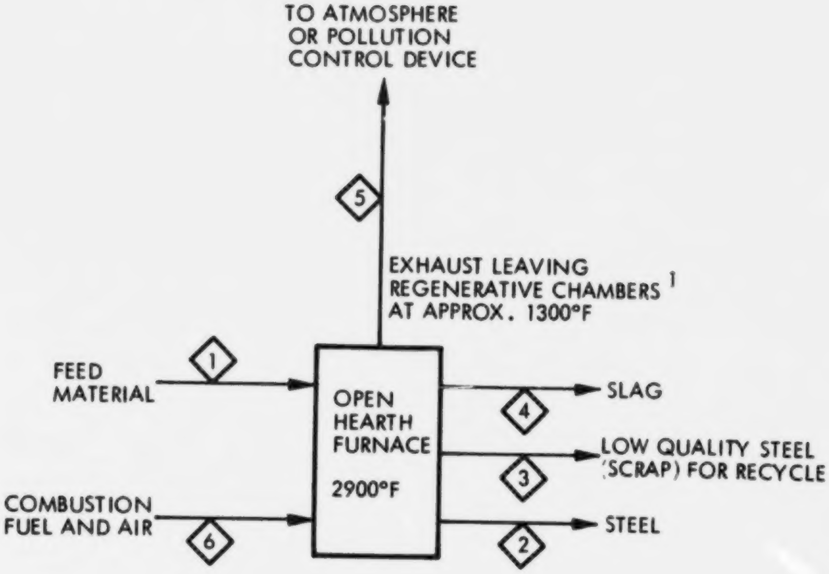
Soluble fluoride evolution factor = 0.81 lb F/ton steel

Note: Fluoride content of the iron ore reflects 95% usage of 650 ppm fluoride content ore and 5% usage of 3000 ppm fluoride content ore.

Figure 3-18. Basic Open Hearth Steelmaking - Uncontrolled Process Model

BASIS

NON-OXYGEN LANCED


TO ATMOSPHERE
OR POLLUTION
CONTROL DEVICE
5
EXHAUST LEAVING
REGENERATIVE CHAMBERS 1
AT APPROX. 1300°F
FEED
MATERIAL
1
OPEN
HEARTH
FURNACE
2900°F
4
SLAG
3
LOW QUALITY STEEL
(SCRAP) FOR RECYCLE
COMBUSTION
FUEL AND AIR
6
2
STEEL

NOTE: (1) IF A WASTE HEAT BOILER IS INSTALLED, THE TEMPERATURE OF THE GASES LEAVING THIS UNIT WOULD BE ABOUT 500°F.

Material
HF
CaF_2
Total Fluorides
Total as F
Pig Iron (Hot)
Scrap
Iron Ore(A)
$CaCO_3$ (Limestone
Raw Steel
Low Quality Stee for Recycle
Slag
N_2
O_2
H_2O
CO_2
SO_2
Fe_2O_3
Air (50% R.H.)
Fuel Oil
Approx. Total Stream

* Gaseous efflue

(A) High fluori
taining 0.09

(B) Reference 40

(C) Reference 80

Soluble fluoride

A

BASIS - FURNACE CAPACITY OF 200 TONS/HEAT - NON OXYGEN LANCED
(2 HEATS PER DAY @ APPROX. 10 HOURS PER HEAT)

PROCESS STREAMS - TONS/HEAT

Material	Stream Number					
	1	2	3	4	5*	6
HF					0.084(g)	
CaF_2	0.33(s)[(B)]			0.17 (s)[(C)]		
Total Fluorides	0.33			0.17	0.084	
Total as F	0.16			0.080	0.080	
Pig Iron (Hot)	100					
Scrap	70					
Iron Ore[(A)]	15					
$CaCO_3$ (Limestone)	15					
Raw Steel		155				
Low Quality Steel for Recycle			5			
Slag				18		
N_2					180(g)	
O_2					5(g)	
H_2O					12(g)	
CO_2					75(g)	
SO_2					0.3(g)	
Fe_2O_3					1(s)[(B)]	
Air (50% R.H.)						235
Fuel Oil						15
Approx. Total Stream	200	155	5	18	270	250

* Gaseous effluent stream

(A) High fluoride content (3000 ppm) ore containing 0.09 tons of CaF_2 equiv.

(B) Reference 4006

(C) Reference 889

Soluble fluoride evolution factor = 1.03 lb. F/ton steel

B

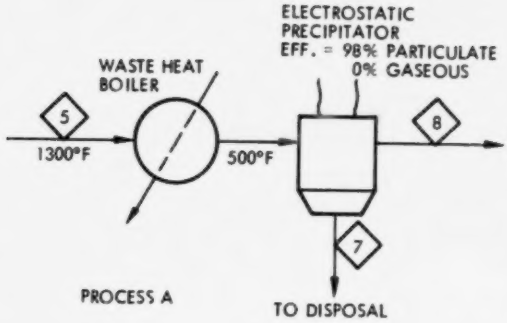
Figure 3-19. Basic Open Hearth Steelmaking Utilizing High Fluoride Content Iron Ore - Uncontrolled Process Model

MBERS 1

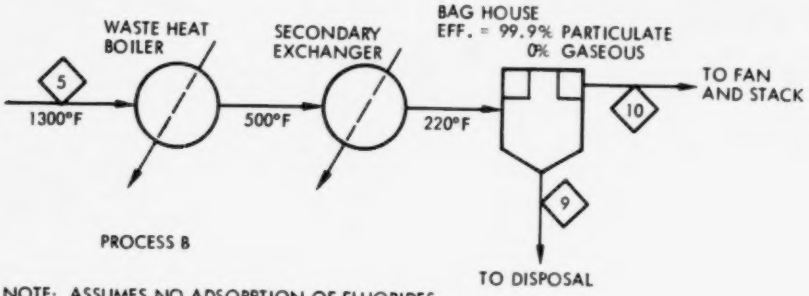
SLAG

LOW QUALITY STEEL
SCRAP) FOR RECYCLE

STEEL


ELECTROSTATIC
PRECIPITATOR
EFF. = 98% PARTICULATE
0% GASEOUS
WASTE HEAT
BOILER
5
1300°F
500°F
8
TO FAN
AND STACK
7
TO DISPOSAL

PROCESS A


WASTE HEAT
BOILER
SECONDARY
EXCHANGER
BAG HOUSE
EFF. = 99.9% PARTICULATE
0% GASEOUS
5
1300°F
500°F
220°F
10
TO FAN
AND STACK
9
TO DISPOSAL

PROCESS B

NOTE: ASSUMES NO ADSORPTION OF FLUORIDES ON PARTICULATE MATTER.

BASIS - FURNACE CAPACITY OF 200 TONS/HEAT - NON-OXYGEN LANCED

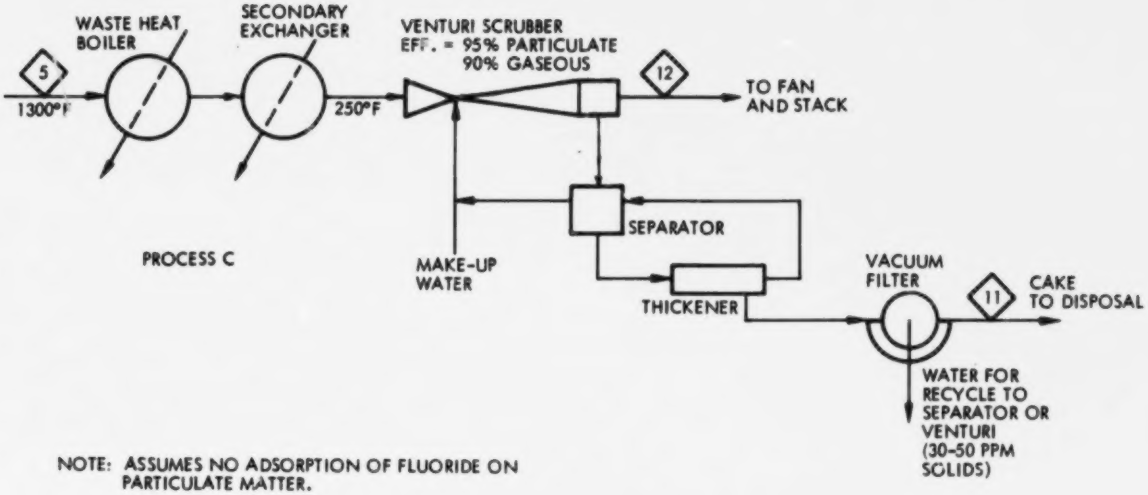
PROCESS STREAMS - TONS/HEAT

Material	Stream Number				
	5	7	8*	9	10*
HF	0.066(g)		0.066(g)		0.066(g)
Total Fluorides	0.066		0.066		0.066
Total as F	0.063		0.063		0.063
N_2	180(g)		180(g)		180(g)
O_2	5(g)		5(g)		5(g)
H_2O	12(g)		12(g)		12(g)
CO_2	75(g)		75(g)		75(g)
SO_2	0.3(g)		0.3(g)		0.3(g)
Fe_2O_3	1(g)	0.98(s)$^{(A)}$	0.02(s)	0.999(s)$^{(A)}$	0.001(s)
Approx. Total Stream	270	1	270	1	270

* Gaseous Effluent Stream

(A) References 4006 and 4055

Figure 3-20. Basic Open Hearth Steelmaking - Controlled Process Model (Processes A and B)


WASTE HEAT BOILER
SECONDARY EXCHANGER
VENTURI SCRUBBER
EFF. = 95% PARTICULATE
90% GASEOUS
5
1300°F
250°F
12
TO FAN AND STACK
SEPARATOR
PROCESS C
MAKE-UP WATER
THICKENER
VACUUM FILTER
11
CAKE TO DISPOSAL
WATER FOR RECYCLE TO SEPARATOR OR VENTURI (30-50 PPM SOLIDS)

NOTE: ASSUMES NO ADSORPTION OF FLUORIDE ON PARTICULATE MATTER.

BASIS - FURNACE CAPACITY OF 200 TONS/HEAT - NON-OXYGEN LANCED

PROCESS STREAMS - TONS/HEAT

Material	Stream Number		
	5	11	12*
HF	0.066(g)	0.059(l)	0.007(g)
CaF_2			
Total Fluorides	0.066	0.059	0.007
Total as F	0.063	0.056	0.0067
N_2	180(g)		180(g)
O_2	5(g)		5(g)
H_2O	12(g)		6(g)
CO_2	75(g)		75(g)
SO_2	0.3(g)		0.03(g)(Est)
Fe_2O_3	1(s)	0.95(s)$^{(B)}$	0.05(s)$^{(B)}$
$Ca(OH)_2$			
Approx. Total Stream	270	1	270

Source	Soluble Fluoride Emission Factor - lb F/ton steel		
	Process A	Process B	Process C
Furnace	0.81	0.81	0.086
Assumed Fugitive	0	0	0
Total Soluble Fluoride Emission Factor	0.81	0.81	0.086

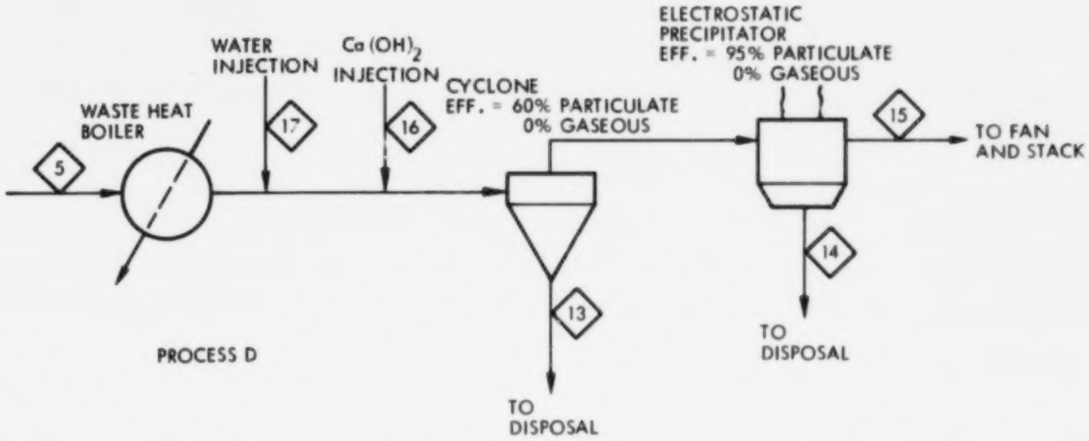
* Gaseous Effluent Stream

Overall process soluble fluoride emission factor = 0.77 lb F/ton steel$^{(A)}$

(A) Reflects estimated 5% usage of high fluoride content (3000 ppm) ore, 95% usage of average fluoride content (650 ppm) ore and application of Process C to 6.1% (Reference 4225) of operating facilities.

(B) References 4006 and 4055

Figure 3-21. Basic Open Hearth Steelmaking - Controlled Process Model (Process C)


ELECTROSTATIC PRECIPITATOR
EFF. = 95% PARTICULATE
0% GASEOUS
WATER INJECTION
Ca(OH)$_2$ INJECTION
CYCLONE
EFF. = 60% PARTICULATE
0% GASEOUS
WASTE HEAT BOILER
17
16
5
15
TO FAN AND STACK
14
13
PROCESS D
TO DISPOSAL
TO DISPOSAL

BASIS - FURNACE CAPACITY OF 200 TONS/HEAT - NON-OXYGEN LANCED

PROCESS STREAMS - TONS/HEAT

Material	Stream Number					
	5	13	14	15*	16	17
HF	0.084			0.004(g)$^{(A)}$		
CaF$_2$		0.094(s)$^{(B)}$	0.059(s)$^{(A)}$	0.002(s)$^{(A)}$		
Total Fluorides	0.084	0.094	0.059	0.006		
Total as F	0.080	0.046	0.029	0.005		
N$_2$	180(g)			180(g)		
O$_2$	5(g)			5(g)		
H$_2$O	12(g)			42(g)$^{(A)}$		30(g)$^{(A)}$
CO$_2$	75(g)			75(g)		
SO$_2$	0.3(g)			0.03(g)(Est)		
Fe$_2$O$_3$	1(s)	0.60(s)$^{(B)}$				
Ca(OH)$_2$		1.3(s)$^{(B)}$	0.76(s)$^{(A)}$	0.04(s)$^{(A)}$	2.1(s)$^{(A)}$	
Approx. Total Stream	270	2	1	270	2	30

* Gaseous Effluent Stream

Soluble fluoride emission factor of facilities utilizing high fluoride content (3000 ppm) iron ore = 0.052 lb F/ton steel

(A) Reference 4053

(B) Reference 4055

Figure 3-22. Basic Open Hearth Steelmaking Utilizing High Fluoride Content Iron Ore - Controlled Process Model

systems. It should be noted that Processes C and D are the only systems currently in use which are capable of abating soluble fluoride emissions from the open hearth furnace. Process C is used to a minor extent only (6.1% of open hearth emission control installations[4225]), and Process D is currently employed only in conjunction with Utah open hearth facilities which charge high fluoride content iron ore to the furnace.

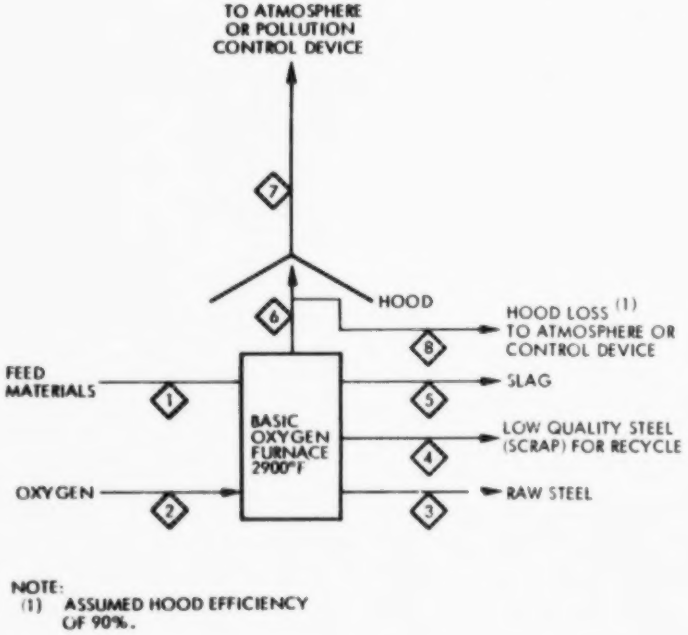
Fluoride Emissions. Soluble fluoride emissions in 1968 from open hearth operations are estimated at 25,400 tons. Fluoride emissions will decline to 0 in 2000 because of the phase-out of open-hearth furnace steel making.

3.3.5.4 Basic Oxygen Furnace Operations

The major materials employed in the basic oxygen steelmaking process (BOF) are pig iron (hot metal), scrap, flux, and gaseous oxygen. The flux is composed of burnt lime (90%) and fluorspar (10%). No external heat is supplied - the heat produced by the reactions between the gaseous oxygen blown into the molten charge and the metals of the charge is sufficient to produce steel. While large quantities of calcium fluoride are volatilized, the absence of any hydrogen source prevents conversion of the volatilized fluoride to gaseous HF. Thus, based on thermochemical equilibrium calculations no measurable quantities of soluble fluorides are emitted by the BOF process. This conclusion should be verified experimentally.

Process Description. Figure 3-23 presents a flow diagram and mass balance for a basic oxygen steelmaking furnace rated with a capacity of 200 tons per heat.

Production Trends. In integrated steel plants, the open hearth furnace has been the predominant steelmaking process, however, the basic oxygen furnace has become increasingly important and in 1970 surpassed the open hearth. (In August 1969 the monthly output of BOFs actually exceeded that of open hearths for the first time.) In nonintegrated plants the open hearth has essentially been displaced by the electric arc furnace.


TO ATMOSPHERE OR POLLUTION CONTROL DEVICE
7
HOOD
6
HOOD LOSS (1) TO ATMOSPHERE OR CONTROL DEVICE
8
FEED MATERIALS
1
BASIC OXYGEN FURNACE 2900°F
5
SLAG
4
LOW QUALITY STEEL (SCRAP) FOR RECYCLE
OXYGEN
2
3
RAW STEEL
NOTE:
(1) ASSUMED HOOD EFFICIENCY OF 90%.

BASIS - FURNACE CAPACITY OF 200 TONS/HEAT
(12 HEATS PER DAY)

PROCESS STREAMS - TONS/HEAT

Materials	Stream Number							
	1	2	3	4	5	6	7*	8*
CaF_2	1.04(s)$^{(C,D)}$				0.51(s)	0.51(s)	0.46(s)	0.05 (s)
Total Fluoride	1.04				0.51	0.51	0.46	0.05
Total as F	.51				0.25$^{(F)}$	0.25$^{(E)}$	0.22	0.025
Pig Iron (Hot)	130							
Scrap	60							
CaO (Burnt Lime)	10							
O_2		11				9(g)	9(g)	1(g)
Low Quality Steel for Recycle				6				
Slag					20			
Raw Steel			165					
CO_2						3(g)	3(g)	0.3(g)
Fe_2O_3						3.3(s)$^{(B)}$	3.3(s)$^{(B)}$	0.3(s)
Approx. Total Stream	200	11	165	6	20	16	16$^{(A)}$	2

* Gaseous effluent stream

(A) Plus 350,000 CFM$^{(6)}$ of dilution air

Soluble Fluoride Evolution Factor = 0 lb F/ton steel produced

(B) Reference 4006

(C) Reference 4246

(D) Reference 4248

(E) Reference 4055

(F) Reference 889

Figure 3-23. Basic Oxygen Steelmaking - Uncontrolled Process Model

In 1954, the first BOF unit was installed in the United States. From levels of only a few million tons in 1960, oxygen steelmaking capacity began to approach installation rates on the order of 10 million tons a year in the mid-1960s, and this nominal rate continues. In 1968, BOF shop accounted for about 37% of U.S. steel production, and their share exceeded 50% in 1970. Many BOF operations have been installed adjacent to comparatively large open hearth shops, to replace or augment open hearth capacity. The BOF process is ideally suited for low-carbon grades, and by the end of 1969 the majority of this steel was produced by the BOF.(4286, 4287) It is expected that BOF production will increase at a rate of 7.6% annually to a constant value of approximately 135 million tons through the year 2000.

Fluoride Emission Control Techniques. Figure 3-24 presents process models and mass balances for currently employed dust and fume control systems.

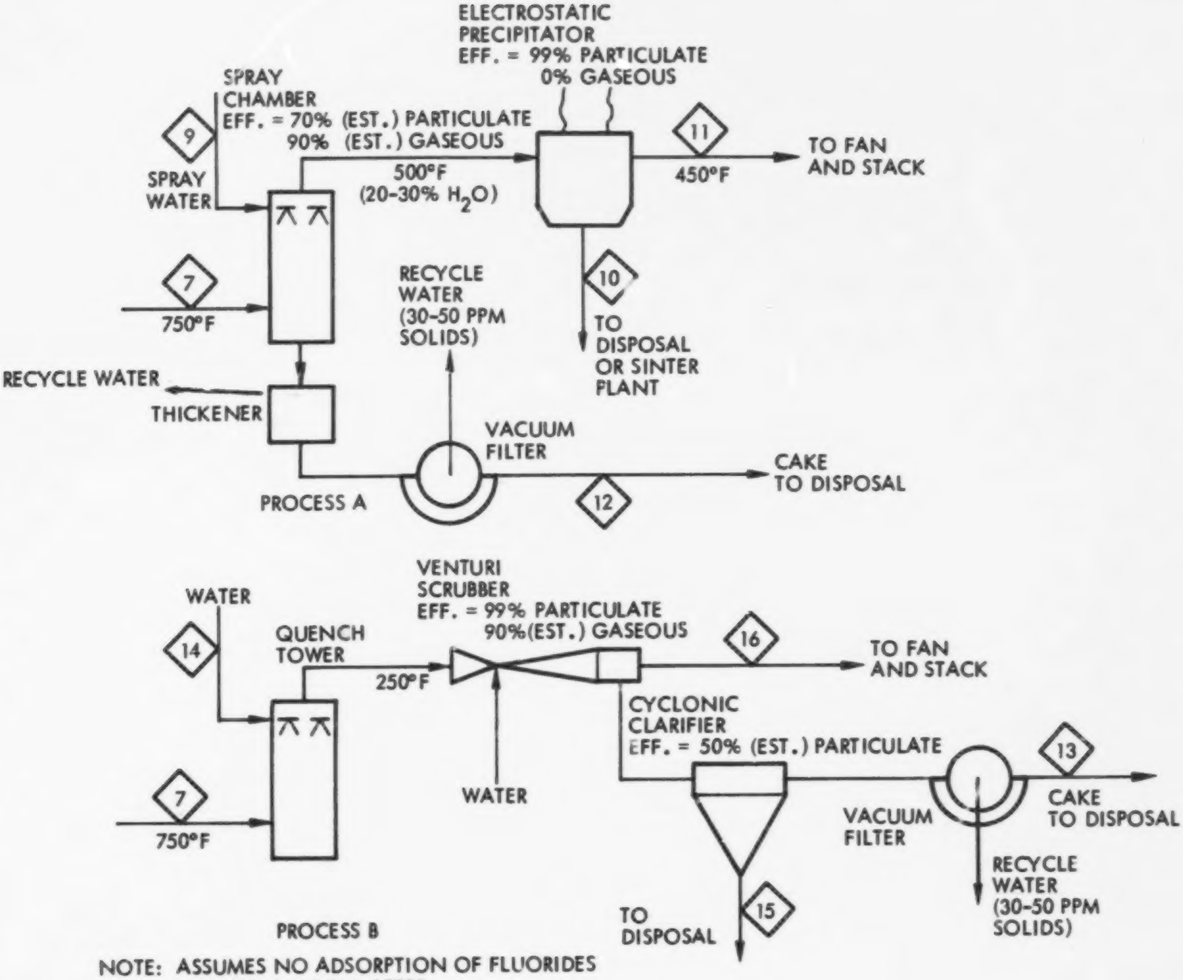
Basic oxygen steel furnaces are hooded by "dust reclaimers" for collection and transport of pollutants to dust control equipment. Gas temperatures may reach 3000° at the collection point.

Fluoride Emissions. Soluble fluoride pollutants from this source are essentially zero since the fluorides emitted are in the form of CaF_2, a relatively harmless insoluble solid. Bases for this conclusion are discussed above.

3.3.5.5 Electric Arc Furnace Operations

Electric arc furnace steelmaking, with two exceptions, does not use hot metal as a part of the charge. The charge materials in the majority of cases, are composed of solid steel scrap of high quality, iron oxide (ore or mill scale), burnt lime, fluorspar, carbon, and gaseous oxygen. The heat necessary is supplied as electrical energy.

Considerable amounts of calcium fluoride are evolved. Because of the absence of a hydrogen source, there is no conversion of any of the evolved calcium fluoride to hydrogen fluoride. Therefore, on the basis of


ELECTROSTATIC PRECIPITATOR
EFF. = 99% PARTICULATE
0% GASEOUS
SPRAY CHAMBER
EFF. = 70% (EST.) PARTICULATE
90% (EST.) GASEOUS
9
SPRAY WATER
500°F
(20-30% H2O)
11
450°F
TO FAN AND STACK
7
750°F
RECYCLE WATER (30-50 PPM SOLIDS)
10
TO DISPOSAL OR SINTER PLANT
RECYCLE WATER
THICKENER
VACUUM FILTER
CAKE TO DISPOSAL
12
PROCESS A
VENTURI SCRUBBER
EFF. = 99% PARTICULATE
90%(EST.) GASEOUS
WATER
14
QUENCH TOWER
250°F
16
TO FAN AND STACK
CYCLONIC CLARIFIER
EFF. = 50% (EST.) PARTICULATE
13
7
WATER
750°F
VACUUM FILTER
CAKE TO DISPOSAL
RECYCLE WATER (30-50 PPM SOLIDS)
TO DISPOSAL
15
PROCESS B

NOTE: ASSUMES NO ADSORPTION OF FLUORIDES ON PARTICULATE MATTER.

Material
CaF_2
Total Fluori Total as F
O_2 CO_2 Fe_2O_3 H_2O
Approx. Total Stream

* Gaseous Eff

(A) Plus 350

(B) Plus req

Overall solub

A

BASIS - FURNACE CAPACITY OF 200 TONS/HEAT (12 HEATS PER DAY)

PROCESS STREAMS - TONS/HEAT

Material	Stream Number								
	7	9	10	11*	12	13	14	15	16*
CaF_2	0.46(s)		0.13(s)$^{(C)}$	0.002(s)$^{(C)}$	0.32(s)	0.23(s)		0.23(s)	0.005(s)$^{(D)}$
Total Fluorides	0.46		0.13	0.002	0.32	0.23		0.23	0.005
Total as F	0.22		0.06	0.001	0.16	0.12		0.12	0.0025
O_2	9(g)			9(g)					9(g)
CO_2	3(g)			3(g)					3(g)
Fe_2O_3	3.3(s)		0.99(s)$^{(C)}$	0.01(s)$^{(C)}$	2.3(s)(Est)	1.7(s)(Est)		1.6(s)(Est)	0.03(s)$^{(D)}$
H_2O		250(l)$^{(B)}$		250(g)		1.7(l)(Est)	80(l)(Est)		80(g)(Est)
Approx. Total Stream	16$^{(A)}$	250$^{(B)}$	1	260$^{(A)}$	2	4	80	2	80$^{(A)}$

Source	Soluble Fluoride Emission Factor lb F/ton steel	
	Process A	Process B
Treated Hood Effluent	0	0
Hood Loss to Atmosphere	0	0
Total Soluble Fluoride Emission	0	0

* Gaseous Effluent Stream

(A) Plus 350,000 CFM of dilution air.

(B) Plus recycle water from vacuum filter.

Overall soluble fluoride emission factor = 0 lb F/ton steel

(C) References 4006 and 2448

(D) References 4006, 2365 and 4055

Figure 3-24. Basic Oxygen Steelmaking - Controlled Process Model

B

thermochemical calculations, calcium fluoride is the only fluoride emitted by the electric arc furnace in measurable quantity.

Process Description. Figure 3-25 presents the process model and mass balances for electric arc steelmaking.

Production Trends. The combination of low capital investment and flexibility in use of scrap has led in the past several years to the increased installation of electric furnace steelmaking shops in areas remote from major steelmaking centers and even more recently in the heart of the steelmaking districts themselves. By locating in areas remote from the major steelmaking centers, a small semi-integrated or nonintegrated shop has several economic advantages. The price of scrap in the local area is lower than in the major steelmaking districts because with no transportation costs it is, in effect, discounted from the standard price; likewise, the products of the local nonintegrated plant also bear no transportation costs and thus can be priced competitively with products shipped to the area from a major steel producing plant. At an integrated steel plant, electric furnace facilities offer the flexibility of easily started peak shaving capacity and the benefits of using in-plant generated scrap unsuitable for charging to the BOF. The electric furnace has great flexibility to produce a wide variety of steels, ranging from low-grade to high-quality steels.

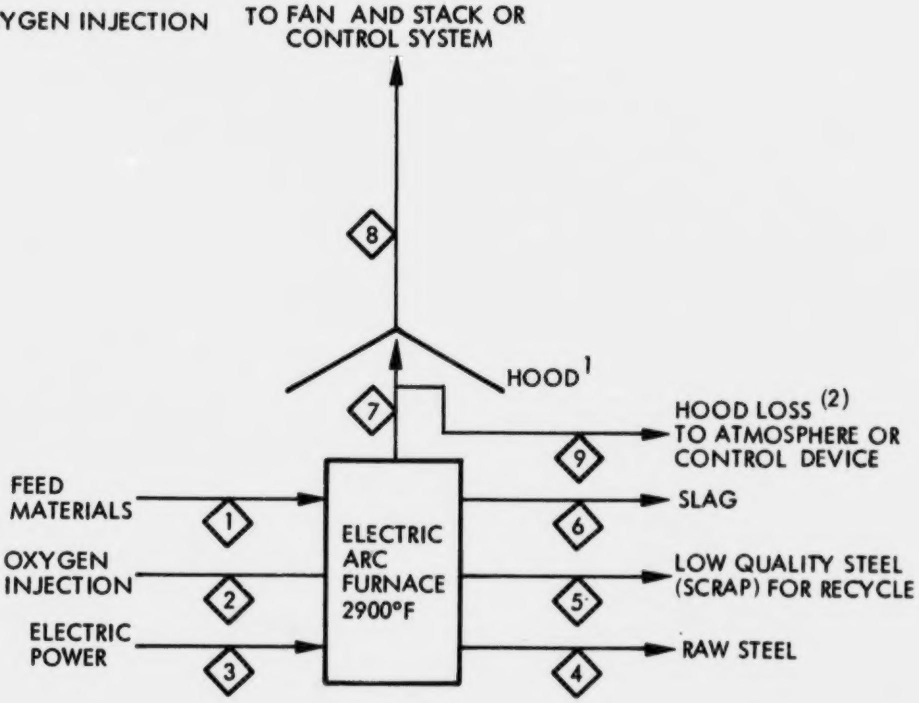
The production of steel by electric arc furnace is expected to grow at a rate of 8.3% (4286, 4287) from a 1968 level of 16 million tons to a constant 35 million tons annually through 2000.

Fluoride Emission Control Techniques. Figure 3-26 presents the process models and mass balances for current processes for electric arc furnace emission control.

Electric arc melting furnaces are hooded in one of three general types: (1) canopy hoods, (2) enclosing or roof-ring hoods, and (3) direct furnace taps. Canopy hoods are located above the crane-way but require large volumes of indraft air to capture furnace effluent efficiently. Roof-ring

BASIS -

WITH OXYGEN INJECTION


TO FAN AND STACK OR CONTROL SYSTEM
8
HOOD[1]
7
HOOD LOSS (2) TO ATMOSPHERE OR CONTROL DEVICE
9
FEED MATERIALS
1
OXYGEN INJECTION
2
ELECTRIC POWER
3
ELECTRIC ARC FURNACE 2900°F
SLAG
6
LOW QUALITY STEEL (SCRAP) FOR RECYCLE
5
RAW STEEL
4

NOTES:

(1) FURNACE EQUIPPED WITH AN INTEGRAL HOOD.

(2) ASSUMED HOOD EFFICIENCY OF 95%.

Materials	
	1
CaF_2	0.3(s)
Total Fluorides	0.3
Total as F	0.15
Steel Scrap	70
Mill Scale	0.5
Carbon (Used Electrodes)	0.3
CaO (Burnt Lime)	3
O_2	
Slag	
Low Quality Steel for Recycle	
CO_2	
Fe_2O_3	
Raw Steel	
Electrical Power	
Approx. Total Stream	75

* Gaseous effluent stream

(A) Plus 150,000 CFM of dilu

Soluble fluoride evolution f

(B) Reference 4006

(C) Reference 4246

(D) Reference 4248

(E) Reference 889

A

BASIS - FURNACE CAPACITY OF 75 TONS/HEAT WITH OXYGEN INJECTION
(4 HEATS PER DAY)

PROCESS STREAMS - TONS/HEAT

Materials	Stream Number								
	1	2	3	4	5	6	7	8*	9*
CaF_2	0.3(s)$^{(C,D)}$					0.14(s)	0.13(s)	0.12(s)	0.01(s)
Total Fluorides	0.3					0.14	0.13	0.12	0.01
Total as F	0.15					0.07	0.07$^{(E)}$	0.06$^{(E)}$	0.007
Steel Scrap	70								
Mill Scale	0.5								
Carbon (Used Electrodes)	0.3								
CaO (Burnt Lime)	3								
O_2		1					0.8(g)	0.8(g)	0.08(g)(Est.)
Slag						5			
Low Quality Steel for Recycle					2				
CO_2							1.1(g)	1.1(g)	0.1(g)(Est.)
Fe_2O_3							0.5(s)	0.5(s)$^{(B)}$	0.05(s)(Est.)
Raw Steel				67					
Electrical Power			160,000KW						
Approx. Total Stream	75	1	-	67	2	5	2.5	2.5$^{(A)}$	0.25

* Gaseous effluent stream

(A) Plus 150,000 CFM of dilution air

Soluble fluoride evolution factor = 0.16 lb F/ton steel produced

(B) Reference 4006

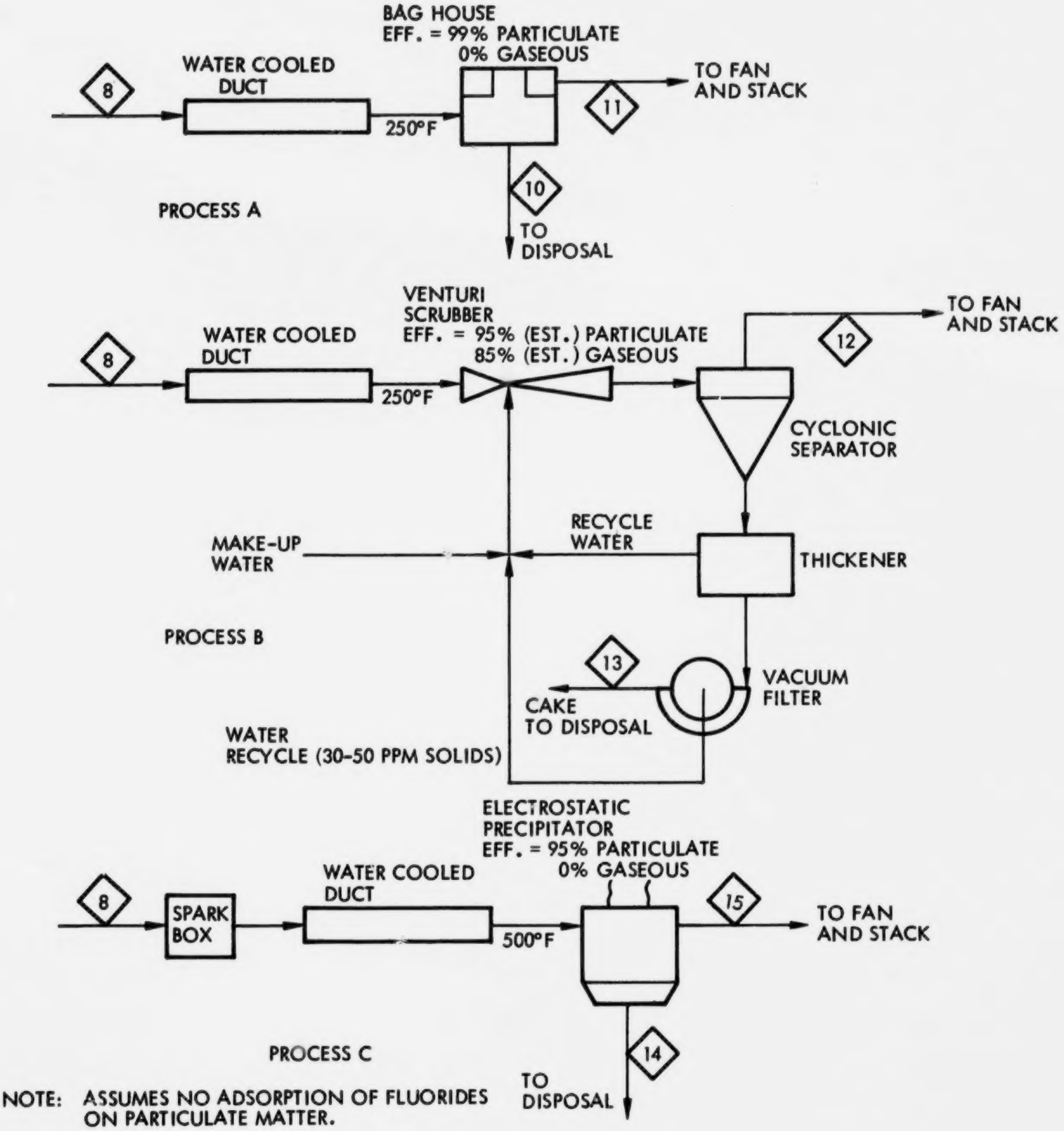
(C) Reference 4246

(D) Reference 4248

(E) Reference 889

B

Figure 3-25. Electric Arc Steelmaking - Uncontrolled Process Model


BAG HOUSE
EFF. = 99% PARTICULATE
0% GASEOUS
8
WATER COOLED DUCT
250°F
11
TO FAN AND STACK
10
TO DISPOSAL
PROCESS A
VENTURI SCRUBBER
EFF. = 95% (EST.) PARTICULATE
85% (EST.) GASEOUS
8
WATER COOLED DUCT
250°F
12
TO FAN AND STACK
CYCLONIC SEPARATOR
MAKE-UP WATER
RECYCLE WATER
THICKENER
PROCESS B
13
CAKE TO DISPOSAL
VACUUM FILTER
WATER RECYCLE (30-50 PPM SOLIDS)
ELECTROSTATIC PRECIPITATOR
EFF. = 95% PARTICULATE
0% GASEOUS
8
SPARK BOX
WATER COOLED DUCT
500°F
15
TO FAN AND STACK
PROCESS C
14
TO DISPOSAL

NOTE: ASSUMES NO ADSORPTION OF FLUORIDES ON PARTICULATE MATTER.

M
CaF_2
Tota
Tota
O_2 CO_2 Fe_2O H_2O
Appr S

*
O
(A
(B

O FAN
ND STACK

BASIS - FURNACE CAPACITY OF 75 TONS/HEAT WITH OXYGEN INJECTION

PROCESS STREAMS - POUNDS/HEAT

Materials	Stream Number						
	8	10	11*	12*	13	14	15*
CaF_2	240(s)	237(s)$^{(B)}$	2(s)$^{(B)}$	12(s)$^{(B)}$	228(s)$^{(B)}$	228(s)$^{(B)}$	12(s)$^{(B)}$
Total Fluorides	240	237	2	12	228	228	12
Total as F	118	115	1	6	111	111	6
O_2	1600(g)		1600(g)	1600(g)			1600(g)
CO_2	2200(g)		2200(g)	2200(g)			2200(g)
Fe_2O_3	1000(s)	990(s)$^{(B)}$	10(g)	50(s)$^{(B)}$	950(s)$^{(B)}$	950(s)$^{(B)}$	50(s)$^{(B)}$
H_2O				100(g)(Est)			
Approx. Total Stream	4900$^{(A)}$	1200	3800$^{(A)}$	3900$^{(A)}$	1200	1200	3900$^{(A)}$

Source	Soluble Fluoride Emission Factor - lb F/ton steel		
	Process A	Process B	Process C
Treated Hood Effluent	0	0	0
Hood Loss to Atmosphere	0	0	0
Total Soluble Fluoride Emission	0	0	0

* Gaseous Effluent Stream

Overall soluble fluoride emission factor = 0 lb F/ton steel

(A) Plus 150,000 cfm of dilution air

(B) References 4006 and 4055

B

Figure 3-26. Electric Arc Steelmaking - Controlled Process Model

hoods and direct furnace tap hoods require the smallest volumes of indraft air for efficient collection. The hot furnace exit gas is cooled via evaporative cooling or radiation coolers and then transported by induced draft to the dust abatement systems shown in the process models.

Fluoride Emissions. No measurable amounts of soluble fluorides are emitted by electric arc furnace operations, based on thermochemical equilibrium calculations.

3.3.6 Economic Analysis

3.3.6.1 Basic Processes

Three specimen cases have been selected for economic analysis as representatives of some of the existing combinations of process elements which occur in the iron and steel industry. These specimen cases are presented in Table 3-24. The steel scrap prices used vary as a function of the types and quantities of scrap required by the process being considered.

Case A, the simplest, is the economic model for an isolated 500,000 ton per year electric furnace steel plant, using steel scrap and finishing additions as the metal charge. Return on investment (equity) for this four-furnace plant, with no fluoride control process, is estimated at 15.3%. After the addition of pollution control equipment currently employed by the industry, return on investment drops to 14.4%.

Case B is the economic model for an integrated iron and steel "division" which purchases pelletized taconite ore, is equipped with coke ovens, produces pig iron in its own blast furnaces, and makes 2 million tons of steel per year in a basic oxygen furnace line. Return on investment prior to use of fluoride control processes is estimated at 7.5%; subsequent to adaption of pollution controls currently employed by the industry, return on investment is estimated at 7.3%.

Table 3-24. Estimated Economics of Electric Furnace Steel Production,[a] Case A (Pollution Control Cost Excluded)

	Plant Capacity[b] 0.5 MM Tons/Year
Total Capital Investment	60.9 $MM
Capital Charges	
Depreciation (at 5% per year)	3.1 $MM/year
Interest (at 7%)	0.9
Local Taxes and Insurance (at 1.5%)	0.9
Total Capital Costs ($MM/year)	4.9
Operating Costs for Electric Furnace Facility	
Steel Scrap (1.068 tons/NTS at 36.00 $/ton[c]	38.45 $/NTS
Finishing Additions (0.007 tons/NTS at $210 (Ave)/ton)	1.47
Electric Power (480 kwh/NTS at $0.007/kwh)	3.36
Electrodes (9.5 lb/NTS at 0.291 $/ton)	2.76
Burnt Lime (0.04 tons/NTS at 16.00 $/ton)	0.64
Refractories	1.60
Oxygen (11 lb/NTS at 12.00 $/NTS)	0.07
Repairs and Maintenance	1.80
Labor (0.8 Man-Hrs/NTS at 5.00 $/Man Hrs)	4.00

Table 3-24. Estimated Economics of Electric Furnace Steel Production,[a] Case A (Pollution Control Cost Excluded) (Continued)

	Plant Capacity 0.5 MM Tons/Year[b]
Utilities	0.45
Yard Switching and Slag Disposal	0.40
Miscellaneous	0.35
General Overhead	0.50
Total Operating Cost for E. F. Facility	55.85 $/NTS
Operating Costs for Continuous Casting	
Billets	
Gross Metallics (1.042 tons molten steel/NTP at 55.85 $/NTS)	58.20 $/NTP
Scrap Credits (0.042 tons scrap/NTP)	(1.14)
Other Costs	7.00
Total Operating Cost for Billets	64.06 $/NTP
Wire Rod	
Continuously Cast Billets (1.075 tons/ton rod at 64.06 $/NTS)	68.86 $/NTP
Scrap Credit (0.065 tons/NTP)	(1.61)
Other Costs	14.75
Total Operating Cost for Wire Rods	82.00 $/NTP
Merchant Bar	
Continuously Cast Billets (1.11 tons/NTP at 64.06 $/NTS)	71.11 $/NTP
Scrap Credit (0.10 tons/NTP)	(2.50)
Other Costs	12.25
Total Operating Cost for Merchant Bar	80.86 $/NTP

Table 3-24. Estimated Economics of Electric Furnace Steel Production,[a] Case A (Pollution Control Cost Excluded) (Continued)

	Plant Capacity[b] 0.5 MM Tons/Year
Total Weighted Average Operating Cost[d] ($/ton)	81.29 $/NTP
Capital Charges Per Net Ton of Final Product (at 0.875 product tons/ton molten steel)	11.20
Total Average Manufacturing Cost	92.49
General and Sales Expenses ($/NTP)	1.85
F.o.b. cost ($/NTP)	94.34
Average Product Revenue[d]	128.50
Profit After Taxes	18.01 $/NTP
Cash Flow	7.88 $MM/year
ROI[e]	15.3%

NTS = Net tons (short) of molten steel
NTP = Net tons product

[a] Semi-integrated plant - four 37.4 (Net tons) electric furnaces, casting machines and mills

[b] Capacity based on molten steel produced

[c] Price may range between 40.00 to 50.00 $/ton

[d] Based on 38% (weight) wire rod and 62% merchant bar production

[e] Return on investors equity (assumed to be 80% of installed capital)

Table 3-24. Estimated Economics of BOF Integrated Steel Production,[a] Case B (Pollution Control Cost Excluded)

	Plant Capacity 2MM Tons/Year[b]
Total Capital Investment	720 $MM
Capital Charges	
Depreciation (at 5%/year)	36.0 $MM/year
Interest (at 7.0%)	10.1
Local Taxes and Insurance (at 1.5%)	10.8
Total Capital Costs ($MM/year)	56.9
Operating Costs for Blast Furnace	
Taconite Pellets (1.6 tons/NTI at 13.70/ton)	21.92 $/NTI
Coke[c] (0.6 tons/NTI at $15.70/ton)	9.42
Limestone (0.26 tons/NTI at 2.05 $/ton)	0.53
Oil (0.04 tons/NTI at 24.88 $/ton)	1.00
Gas Credit	(0.71)
Dust and Sludge Credit	(0.06)
Labor (0.1 Man-Hrs/NTI at 5.00 $/Man-Hr)	0.50
Utilities	1.00
Refractories	0.15
Reline Costs	0.60
Maintenance and Repair	0.75
Miscellaneous Supplies	0.78
General Overhead	0.45
Total Blast Furnace Operating Cost	36.33 $/NTI

Table 3-24. Estimated Economics of BOF Integrated Steel Production,[a] Case B (Pollution Control Cost Excluded) (Continued)

	Plant Capacity 2MM Tons/Year[b]
Operating Costs for a Basic Oxygen Facility	
Hot Metal (0.8 tons/NTS at 36.33 $/ton)	29.06 $/NTS
Steel Scrap (0.34 tons/NTS at 26.50 $/ton)	9.01
Finishing Additions (0.007 tons/NTS at APX 210 $/ton)	1.47
Burnt Lime (130 lb/NTS at $16.00/ton)	1.04
Refractories	1.40
Oxygen (148 lb/NTS at 12.00 $/ton)	0.89
Labor (0.6 Man-Hrs at 5.00 $/Man-Hr)	3.0C
Repairs and Maintenance	2.88
Utilities	0.40
Yard Switching and Slag Disposal	0.45
Miscellaneous Supplies and Services	0.40
General Overhead	0.50
Total Operating Cost for BOF Facility	50.50 $/NTS
Operating Costs for Continuous Casting	
Slabs	
Gross Metallics (1.042 tons molten steel/NTP at $50.50/NTS)	52.60 $/NTP
Scrap Credits (0.042 tons scrap/NTP)	(1.00)$/NTP
Other Costs	6.00
Total Operating Cost for Slabs	57.60
Hot-Rolled Sheets	
Slabs (1.11 tons/NTP at 57.60 $/NTS)	63.93/NTP
Scrap (0.087 tons/NTP)	(2.15)
Other Costs	11.09
Total Operating Cost for Hot-Rolled Sheets	72.87 $/NTP

Table 3-24. Estimated Economics of BOF Integrated Steel Production,(a) Case B (Pollution Control Cost Excluded) (Continued)

	Plant Capacity 2MM Tons/Year(b)	
Cold-Rolled Coils (Annealed and Tempered)		
Slabs (1.142 tons/NTP at 57.60 $/NTS	65.76	$/NTP
Scrap (0.035 tons/NTP)	(3.40)	
Other Costs	20.63	
Total Operating Cost for Hot Rolled Sheets	82.99	$/NTP
Cold-Rolled Sheets		
Slabs (1.202 tons/NTP at 57.60 $/NTS)	69.29	$/NTP
Scrap Credit (0.06 tons/NTP)	(4.91)	
Other Costs	25.67	
Total Operating Cost for Cold-Rolled Sheets	90.05	$/NTP
Total Weighted Average Operating Cost (d) ($/ton)	81.85	$/NTP
Capital Charges Per Net Ton of Final Product (0.837 product tons/ton molten steel)	33.99	$/NTP
Total Average Manufacturing Cost (d)	115.84	
General and Sales Expenses ($/NTP)	2.32	
F.o.b. Cost ($/NTP)	118.16	
Average Product Revenue(d)	169.91	
Profit After Taxes (Tax at 50%)	25.88	$/NTP
Cash Flow	79.3	$MM/year
ROI(e)	7.5%	

NTI = net tons (short) iron

(a) Integrated plant - coke ovens, blast furnace, steelmaking furnaces (BOF), casting machines and mills

(b) Based on molten steel production

(c) Assume: 1.44 tons low S coal/ton (coke), $4.73/ton credit and $ 6.00/ton operating costs

(d) Based on 28% (weight) hot rolled sheets, 48% annealed and tempered cold rolled coils and 24% cold rolled sheets produced

(e) Return on investors equity (assuming equity is 80% of installed capital)

Table 3-24. Estimated Economics of OH Integrated Steel Production,[a] Case C (Pollution Control Cost Excluded)

	Plant Capacity 2MM Tons/Year[b]
Total Capital Investment	742 $MM
Capital Charges	
Depreciation (at 5%/year)	37.1
Interest (at 7%)	10.4
Local Taxes and Insurance (at 1.5%)	11.1
Total Capital Cost ($MM/year)	58.6
Operating Costs for Sintering	
Mesabi Iron Ore (0.95 tons/ton sinter at $10.60/ton)	10.07 $/ton sinter
Limestone (0.06/ton sinter at $2.05/ton)	0.13
Coke[c] (0.25 tons/ton sinter at $15.70/ton)	3.93
Water (5.0 gal/ton sinter at $0.08/1000 gal)	0.01[d]
Natural Gas (400 scf/ton at $0.35/1000 scf)	0.14
Dust Credit	(0.30)
Labor (0.1 man-hr/ton sinter at $5.00 /Man-Hr)	0.50
Utilities	0.60
Maintenance	1.00
Miscellaneous Supplies	0.40
General Overhead	0.40
Total Sintering Operating Cost	16.88 $/ton sinter
Operating Costs for Blast Furnace	
Sinter (1.15 tons/NTI at $16.88/ton)	19.44 $/NTI
Screened Ore (0.4 tons/NTI at $10.60/ton)	4.19

Table 3-24. Estimated Economics of OH Integrated Steel Production,[a] Case C (Pollution Control Cost Excluded) (Continued)

	Plant Capacity 2MM Tons/Year[b]
Coke[c] (0.52 tons/NTI at \$15.70/ton)	8.05
Limestone (0.06 tons/NTI at \$2.05/ton)	0.13
Natural Gas (1 scf/NTI at \$0.35/1000 scf)	0.01[d]
Gas Credit (4850 pounds)	(0.71)
Dust and Sludge Credit	(0.06)
Labor (0.1 Man-Hr/NTI at \$5.00/Man-Hr)	0.50
Utilities	1.00
Refractories	0.15
Reline Costs	0.60
Maintenance and Repair	0.75
Miscellaneous Supplies	0.78
General Overhead	0.45
Total Blast Furnace Operating Cost	35.28 \$/NTI
Operating Costs for an Open-Hearth Facility	
Hot Metal (0.66 tons/NTS at \$35.28/NTI)	23.20 \$/NTS
Scrap Steel (0.44 tons/NTS at \$36.00/ton)	15.77
Ferro Alloys (0.00 7 tons/NTS at Apx \$210/ton)	1.47
Flux (0.09 ton CaF_2/NTS at \$65.00/ton)	5.85
Iron Ore (0.1 ton ore/NTS at \$10.60/ton)	1.06
Fuel Oil (0.09 ton oil/NTS at \$24.88/ton)	2.24
Labor (0.5 Man-Hr at \$5.00/Man-Hr)	2.50

Table 3-24. Estimated Economics of OH Integrated Steel Production,(a) Case C (Pollution Control Cost Excluded) (Continued)

	Plant Capacity 2MM Tons/Year(b)
Maintenance	3.00
Utilities	0.40
Switching and Slag Disposal	0.50
Miscellaneous Supplies and Services	0.40
General Overhead	0.50
Total Operating Cost for OH Facility	56.89
Slabs	
Gross Metallics (1.042 tons molten steel/NTP at 56.89/NTS)	59.28 $/NTP
Scrap Credits (0.042 tons scrap/NTP)	(1.00)$/NTP
Other Costs	6.00
Total Operating Cost for Slabs	64.28
Hot-Rolled Sheets	
Slabs (1.11 tons/NTP at 64.28 $/NTS)	71.35 NTP
Scrap (0.087 tons/NPT)	(2.15)
Other Costs	11.09
Total Operating Cost for Hot-Rolled Sheets	80.29 $/NTP
Cold-Rolled Coils (Annealed and Tempered)	
Slabs (1.142 tons/NTP at 64.28 $/NTS)	73.41 $/NTP
Scrap (0.035 tons/NTP)	(3.40)
Other Costs	20.63
Total Operating Cost for Hot Rolled Sheets	90.64 $/NTP

Table 3-24. Estimated Economics of OH Integrated Steel Production,[a] Case C (Pollution Control Cost Excluded) (Continued)

	Plant Capacity 2MM Tons/Year[b]
Cold-Rolled Sheets	
Slabs (1.202 tons/NTP at 64.28 $/NTS)	77.26 $/NTP
Scrap Credit (0.06 tons/NTP)	(4.91)
Other Costs	25.67
Total Operating Cost for Cold Rolled Sheets	98.74 $/NTP
Total Weighted Average Operating Cost[e] ($/ton)	89.69 $/NTP
Capital Charges Per Net Ton Final Product (at 0.837 tons product/ton molten steel)	35.01
Total Average Manufacturing Cost[e]	124.70
Average Product Revenue[e]	169.91
General and Sales Expenses ($/NTP)	2.49
F.o.b. Cost ($/NTP)	127.19
Profit After Taxes (Tax at 50%)	21.36 $/NTP
Cash Flow	72.9 $MM/year
ROI[f]	6.0%

[a] Integrated plant - coke ovens, sintering, blast furnace, steelmaking furnaces (OH), casting machines and mills

[b] Based on molten steel production

[c] Assume: 1.44 tons low S coal/ton coke, $4.73/ton credit and $6.00/ton operating costs

[d] Conservative estimate

[e] Based on 28% hot rolled sheets, 48% annealed and tempered cold rolled coils and 24% cold rolled sheets

[f] Return on investors equity (taken at 80% of installed capital)

NTI = Net tons iron produced
NTS = Net tons steel produced

Case C covers economic analyses of an integrated iron and steel division, producing 2 million tons per year of steel from open hearth furnaces. Operating facilities in addition to the open hearth furnaces at the division include coke ovens, an ore-sintering plant and blast furnaces for hot metal (pig iron) production. Return on investment, without addition of fluoride control processes, is estimated at 6.0%. After pollution control equipment currently employed by the industry is added, return on investment drops to 5.8%.

In actual practice, a single iron and steel facility usually contains a coke plant, a sintering plant, blast furnaces and a number of open hearth, electric arc, and basic oxygen steel making furnaces. Return on investment for a facility of this type, before addition of fluoride control process costs, is estimated at 7.7%. After addition of pollution control equipment currently employed by the industry, the facility is estimated to return 7.5% on investment.

The relative reduction on return of investment for the four cases discussed above is presented in Figure 3-27. Plant and division locations, for modeling purposes, are assumed to be in the Great Lakes area of Ohio. The general process economic assumptions contained in Section 3.1.1 were used in developing the estimates for the iron and steel industry.

The industry, or for that matter, an individual company's return on investment is difficult to establish clearly. Net income (after taxes) for any one firm may vary substantially from year to year as the result of a number of related factors. Heavy "start-up" costs for major investments, close economic ties to a single industry (e.g., automobiles), imported steel products, stockpiling of steel in strike years, production rates, accounting practices (inventory accounting systems or change from accelerated to straight-line depreciation schedules) and obsolete plant equipment carried on the "books" may all substantially change the return on investment calculation.

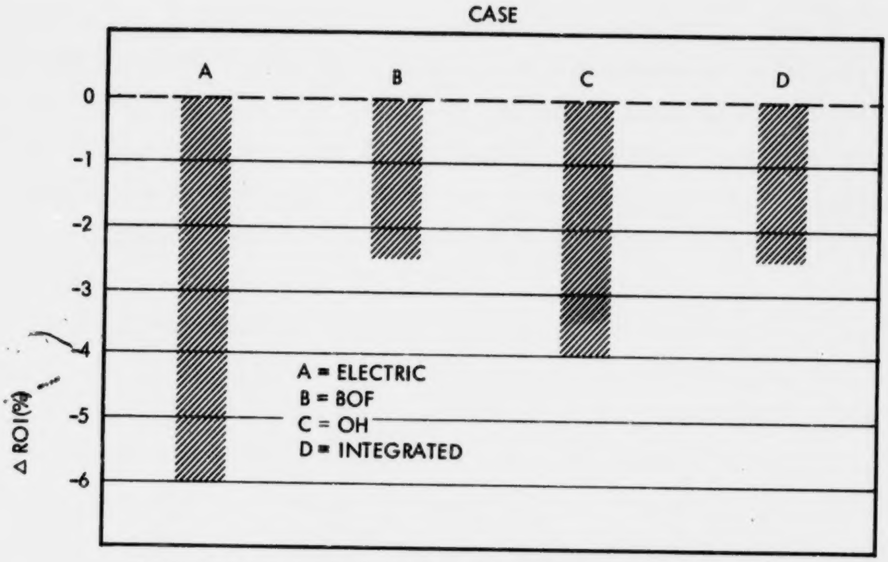


Figure 3-27. Relative Reduction on Return on Investment (ROI) for Iron and Steel Industry

3.3.6.2 Impact of Controls

The individual process element pollution control cost analyses sheets for the systems currently employed by the industry, which are presented below, may be summarized as follows for the three specimen cases:

Case A: The annual cost of systems currently employed for control of emissions from the 500,000 ton per year electric arc furnace plant is estimated at $280,000 per year, equivalent to $0.64 per ton of steel product.

Case B: The annual cost of systems currently employed for control of emissions from the integrated iron and steel "division" using purchased pelletized ore and producing steel in basic oxygen furnaces is estimated at $885,000 per year, equivalent to $0.56 per ton of steel.

Case C: The annual cost of systems currently employed for control of emissions from the integrated iron and steel "division" sintering its ore and producing steel in open hearth furnaces is estimated as $1,390,000 per year, equivalent to $0.83 per ton of steel.

Most of the systems currently employed for control of emissions were installed solely for control of particulate discharges, and control soluble fluoride emissions incidentally, if at all. The dry collection devices remove none of the gaseous fluorides evolved. The costs of emission control given above involve control of soluble fluorides only to the extents noted in the controlled process diagrams; no soluble fluorides are evolved or emitted by the basic oxygen and electric arc furnace processes.

The iron and steel industry is generally assumed to be subject to oligopolistic competition; that is, prices are usually set by the largest firms with smaller firms following the pattern thus established. For this type of competition, prices tend to hold without much change for considerable periods even in the face of fluctuating demand and increasing cost pressures, such as the current labor contract settlement. This suggests that different firms will be required to absorb a greater share of the cost of fluoride pollution control than others and that the cost differential will not be reflected in price competition.

Because of the extensive anti-inflationary pressure on the iron and steel industry, the basic unit sale price must be assumed to be constant. Thus, the total burden of the control costs will probably rest on the stockholders of the firms. This would mean that the full reduction in return on investment would be felt and the firms' cash generating capability decreased.

Iron Ore Sintering. Economic analyses of the control processes for normal fluoride content ore are presented in Tables 3-25 through 3-27. Costs range from $0.13 to $0.21 per ton for normal fluoride content ore; costs for high fluoride content ore are $0.93 per ton of sinter.

Blast Furnace.

Control Economics. Table 3-28 covers analysis of the costs of current fluoride control processes for normal and high fluoride content iron ore. Estimated cost for "normal' ore is $0.32 per ton of pig iron.

Table 3-25. Iron Ore Sintering - Estimated Economics of Control Process A
Basis - 2000 Tons/Day of Sinter Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Cyclone, 460,000 cfm, 4.9 in. Wg pressure drop, low alloy steel, 26.4 lb/min loading, 350°F, 475 hp	186	4387	2.82		524
2	Electrostatic Precipitator, 375,000 cfm, 0.9 in. WG pressure drop, low allow	286	(a)	1.69		483
					Capital Subtotal	1,007
					Indirects (@ 15%)	151
					Contingency (@ 20%)	201
					Total Capital (as of January 1971)	1,359

(a) See footnote 20.

All control economics footnotes are located in Section 3.1.1pages 3-10 and 3-11

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	2.48	0.13		2.61
2	1.58	0.38		1.96
Subtotal				4.57
Water(21)				-
Disposal(22)				-
Total Operating Cost				4.57

Total Operating Cost ($/hr)	4.57
Taxes and Insurance (2%, 330 days)	3.43
Capital (7.1%, 330 working days)	9.60
Pollution Control Cost ($/hr)	17.60
Pollution Control Cost ($/ton)	0.21

Table 3-26. Iron Ore Sintering - Estimated Economics of Control Process B
Basis - 2000 Tons/Day of Sinter Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Cyclone, 225,000 cfm, 4.9 in. WG pressure drop, low alloy steel, 232 hp.	103	4387 4390 4392	2.82		290
2	Electrostatic Precipitator 210,000 cfm, 0.9 in. WG pressure drop	193	(a)	1.69		326
	(a) See footnote 20.					
				Capital Subtotal		616
				Indirects (@ 15%)		92
				Contingency (@ 20%)		123
				Total Capital (as of January 1971)		831

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	1.21	0.13		1.34
2	0.88	0.38		1.26
Subtotal				2.60
Water(21)				-
Disposal(22)				-
Total Operating Cost				2.60

Total Operating Cost ($/hr)	2.60
Taxes and Insurance (2%, 330 days)	2.10
Capital (7.1%, 330 working days)	5.88
Pollution Control Cost ($/hr)	10.58
Pollution Control Cost ($/ton)	0.13

Table 3-27. Iron Ore Sintering - Estimated Economics of Control Process C
Basis - 2000 Tons/Day of Sinter Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Cyclone, 225,000 cfm, 4.9 in. WG pressure drop, low alloy steel, 232 hp.	77	4387 4390 4392	2.66		205
2	Spray Scrubber, 2 at 14 ft by 30 ft, 8 ft/sec allowable velocity, 148,000 cfm, 80 moles/(hr) (ft^3) (atm) mass transfer coefficient, 2 in. WG pressure drop, neoprene lined steel, 62 hp.	138	4387 4388 4390 4391	2.58		356
3	Thickener, 5000 gal per min, 31 lb/min loading, 100,000 gal capacity, neoprene lined steel	42	4383 4392	2.36		99
4	Vacuum Filter, 100 ft^2 area, 31 lb/min, 5000 gal/min, 38 hp required.	78	4383 4392	2.70		168
					Capital Subtotal	828
					Indirects (@ 15%)	124
					Contingency (@ 20%)	166
					Total Capital (as of January 1971)	1,118

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	1.21	0.13		1.44
2	0.32	0.25		0.74
3	–	0.06		0.06
4	0.20	0.33		0.53
Subtotal				2.77
Water(21)		(700 gpm, 90% recycle)		0.57
Disposal(22)				–
Total Operating Cost				3.34

Total Operating Cost ($/hr)	3.34
Taxes and Insurance (2%, 330 days)	2.82
Capital (7.1%, 330 working days)	7.91
Pollution Control Cost ($/hr)	14.07
Pollution Control Cost ($/ton)	0.17

Table 3-28. Pig Iron Production - Estimated Economics of Control Process
Basis - 1000 Tons Pig Iron Per Day

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Cyclone, 140,000 cfm, 4.9 in. WG pressure drop, 145 hp required, low alloy steel.	49	4387 4390	2.80		137
2	Wet Scrubbers, 2 at 14 ft by 24 ft, 1.6 in. WG pressure drop, 3040 gpm liquid rate, 8 ft/sec allowable velocity, 80 moles/(hr) (ft^3) (atm) mass transfer coefficient, neoprene lined steel, 94 hp.	95	4387 4388 4390 4391	2.53		240
3	Thickener, 3100 gpm, 12.5 lb/min loading, 62,000 gal capacity, neoprene lined steel.	28	4383 4392	2.36		66
4	Vacuum Filter, 60 ft^2, 3100 gpm, 12.5 lb/min loading, 63 hp, neoprene lined steel.	52	4383 4392	2.15		112
5	Electrostatic Precipitator, 105,000 cfm, 0.9 in. WG pressure drop.	116	(a)	1.69		196
				Capital Subtotal		751
				Indirects (@ 15%)		113
				Contingency (@ 20%)		150
				Total Capital (as of January 1971)		1,014

(a) See footnote 20.

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.76	0.13		0.89
2	0.49	0.50		0.99
3	–	0.06		0.06
4	0.33	0.14		0.47
5	0.57	0.16		0.73
Subtotal				3.14
Water(21)	(3100 gpm, 90% recycle)			0.37
Disposal(22)				–
Total Operating Cost				3.51

Total Operating Cost ($/hr)	3.51
Taxes and Insurance (2%, 330 days)	2.56
Capital (7.1%, 330 working days)	7.17
Pollution Control Cost ($/hr)	13.24
Pollution Control Cost ($/ton)	0.32

Open Hearth Furnace

Control Economics. Tables 3-29 through 3-32 present analyses of costs for the processes currently employed for control of emissions from open hearth operations. Implementation of new control systems may be hard to justify, due to the proposed phase-out of the open hearth.

Basic Oxygen Furnace

Control Economics. Tables 3-33 and 3-34 present current emission control process costs for BOF steelworking.

Electric Arc Furnace

Control Economics. Tables 3-35, 3-36, and 3-37 present the cost of control of emissions from electric arc furnaces.

Table 3-29. Basic Open Hearth Steelmaking(24) - Estimated Economics of Control Process A
Basis - Furnace Capacity of 200 Tons/Heat (2 Heats Per Day @ Approx. 10 Hours Per Heat)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Waste Heat Boiler, 2000 ft^2 surface area, assumed Δt_m = 241° and $U\Delta t$ = 4,800 Btu/hr/ft^2, 33,000 cfm, t_{in} = 1300°F, t_{out} = 500°F, 20 in. WG pressure drop, low alloy steel, 340 hp.	33	4392	3.09		102
2	Electrostatic Precipitator, 20,000 cfm, 0.9 in. WG pressure drop.	56	(a)	1.69		95
				Capital Subtotal		197
				Indirects (@ 15%)		30
				Contingency (@ 20%)		39
				Total Capital (as of January 1971)		266

(a) See footnote 20.

All control economics footnotes are located in Section 3-1.1 pages 3-10 and 3-11

Operating Cost ($ /heat)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	10.26	1.32		11.58
2	0.84	4.56		5.40
Subtotal				16.98
Water(21)				-
Disposal(22) (1 ton/heat of Fe_2O_3)				0.50
Total Operating Cost				17.48

Total Operating Cost ($/heat)	17.48
Taxes and Insurance (2%, 330 days)	8.06
Capital (7.1%, 330 working days)	22.57
Pollution Control Cost ($/heat)	48.31
Pollution Control Cost ($/ton)	0.24

Table 3-30. Basic Open Hearth Steelmaking(24) - Estimated Economics of Control Process B
Basis - Furnace Capacity of 200 Tons/Heat (2 Heats Per Day @ Approx. 10 Hours Per Heat)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Waste Heat Boiler, 2000 ft^2 surface area, Δtm = 241° and $U\Delta tm$ = 4800 Btu/hr/ft^2, 33,000 cfm t_{in} = 1300°F, t_{out} = 500°F, low allov steel, 20 in. WG pressure drop, 340 hp.	33	4383 4392	3.09		102
2	Secondary Exchanger, 1650 ft^2 surface area, V = 25 Btu/hr/ft^2-°F, $U\Delta tm$ = 1944 Btu/hr/ft^2, 20,000 cfm, t_{in} = 500°F, t_{out} = 220°F, steel, 20 in. WG pressure drop, 84 hp.	27	4383 4392	3.07		83
3	Baghouse, 13000 cfm, 3.34 lb/min loading, 2.5 in. WG pressure drop, fabric felter-shaker, 7 hp.	13	4387 4383	4.13		54
				Capital Subtotal		239
				Indirects (@ 15%)		36
				Contingency (@ 20%)		48
				Total Capital (as of January 1971)		323

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Operating Cost ($ / heat)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	10.26	1.32		11.58
2	4.40	1.20		5.60
3	0.36	15.12		15.48
Subtotal				32.66
Water(21)				-
Disposal(22)		(1 ton Fe_2O_3/heat)		0.50
Total Operating Cost				33.16

Total Operating Cost ($/heat)	33.16
Taxes and Insurance (2%, 330 days)	9.79
Capital (7.1%, 330 working days)	27.41
Pollution Control Cost ($/heat)	70.36
Pollution Control Cost ($/ton)	0.35

Table 3-31. Basic Open Hearth Steelmaking(24) - Estimated Economics of Control Process C
Basic - Furnace Capacity of 200 Tons/Heat (2 Heats Per Day @ Approx. 10 Hours Per Heat)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Waste Heat Boiler, 2000 ft^2 surface area, Δtm = 241° and $U\Delta tm$ = 4800 Btu/hr/ft^2, 33,000 cfm, t_{in} = 1300°F, t_{out} = 500°F, 20 in. WG pressure drop, 340 hp, low alloy steel.	33	4383 4392	3.09		102
2	Secondary Exchanger, 1650 ft^2 surface area, V = 25 Btu/hr/ft^2-°F, 20,000 cfm, t_{in} = 500°F, t_{out} = 220°F, 20 in. WG pressure drop, 84 hp, carbon steel.	27	4383 4392	3.07		83
3	Venturi Scrubber, 130,000 cfm, monel clad, 3.34 lb/min loading, 110 gpm, neoprene lined steel, 31.5 in. WG pressure drop, 86 hp.	32	4383 4390 4391	1.75		56
4	Separator, 1000 gal capacity, neoprene lined steel.	6		3.5		21
5	Thickener, 10,000 gal capacity, 3.17 lb/min loading.	17	4383	2.35		40
6	Vacuum Filter, 3.2 lb/min loading, neoprene lined steel, 100ft^2, 38hp	78	4383	2.17		169
				Capital Subtotal		471
				Indirects (@ 15%)		71
				Contingency (@ 20%)		94
				Total Capital (as of January 1971)		636

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Operating Cost ($ / heat)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	10.26	1.32		11.58
2	4.40	1.2		5.60
3	4.50	1.56		6.06
4	0.12	0.60		0.72
5	1.98	0.76		2.74
Subtotal				26.70
Water(21)	(110 gpm, 90% recycle)			0.13
Disposal(22)	(1 ton Fe_2O_3/heat)			0.50
Total Operating Cost				27.33

Total Operating Cost ($/heat)	27.33
Taxes and Insurance (2%, 330 days)	19.27
Capital (7.1%, 330 working days)	53.96
Pollution Control Cost ($/heat)	100.56
Pollution Control Cost ($/ton)	0.50

Table 3-32. Basic Open Hearth Steelmaking(24) - Estimated Economics of Control Process D Basis - Furnace Capacity of 200 Tons/Heat (2 Heats Per Day @ Approx. 10 Hours Per Heat)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Waste Heat Boiler, 2000 ft^2 surface area, $\Delta t_m = 241°$, $U\Delta t_m = 4800$ Btu/hr/ft^2, 33,000 cfm, $t_{in} = 1300°F$, $t_{out} = 500°F$, 20 in. WG pressure drop, 340 hp, low alloy steel.	33	4383 4392	3.09		102
2	Cyclone, 22,000 cfm, 4.9 in. WG pressure drop, low alloy steel.	15	4390 4387	2.8		42
3	Electrostatic Precipitator, 21,000 cfm, 0.9 in. WG pressure drop.	56	(a)	1.69		95
	Capital Subtotal					239
	Indirects (@ 15%)					36
	Contingency (@ 20%)					48
	Total Capital (as of January 1971)					323

(a) See footnote 20.

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Operating Cost ($ /heat)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	10.26	1.32		11.58
2	1.19	1.52		2.71
3	0.88	4.55		5.43
Subtotal				19.72
Water(21) (15 gpm)				0.17
Disposal(22) (3 tons $Ca(OH)_2$, Fe_2O_3 and CaF_2/heat)				1.50
Slaked Lime(25) (0.21 tons $Ca(OH)_2$/heat)				1.30
Total Operating Cost				22.69

Total Operating Cost ($/heat)	22.69
Taxes and Insurance (2%, 330 days)	9.79
Capital (7.1%, 330 working days)	27.41
Pollution Control Cost ($/heat)	59.89
Pollution Control Cost ($/ton)	0.30

Table 3-33. Basic Oxygen Steelmaking(19) - Estimated Economics of Control Process A
Basis - Furnace Capacity of 200 Tons/Heat (12 Heats Per Day)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Spray Chambers, 5 at 14 ft dia by 26 ft, 358,000 cfm, 8 ft/sec allowable velocity, 2 in. WG pressure drop, 151 hp, mass transfer coefficient of 80 moles/(hr) (ft^3) (atm), carbon steel	125	4386 4388 4390 4391	3.73		466
2	Thickener, 7800 gpm, 34 lb/min. 160,000 gal capacity, carbon steel.	28	4383	3.57		100
3	Vacuum Filter, 7800 gal/min, 160 ft^2, 34 lb/min loading, carbon steel, 61 hp.	59	4383	3.22		190
4	Electrostatic Precipitator, 270,000 cfm, 0.9 in. WG pressure drop.	220	(a)	1.69		372
				Capital Subtotal		1,128
				Indirects (@ 15%)		159
				Contingency (@ 20%)		226
				Total Capital (as of January 1971)		1,523

(a) See footnote 20.

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Operating Cost ($ /heat)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	1.58	2.50		4.08
2	—	0.12		0.12
3	0.64	0.66		1.30
4	2.27	0.76		3.03
Subtotal				8.53
Water(21) (7770 gpm, 90% recycle)				0.94
Disposal(22)				—
Total Operating Cost				9.47

Total Operating Cost ($/heat)	9.47
Taxes and Insurance (2%, 330 days)	7.69
Capital (7.1%, 330 working days)	23.11
Pollution Control Cost ($/heat)	40.27
Pollution Control Cost ($/ton)	0.20

Table 3-34. Basic Oxygen Steelmaking(19) - Estimated Economics of Control Process B
Basis - Furnace Capacity of 200 Tons/Heat (12 Heats Per Day)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Quench Towers, 4 at 14 ft dia by 20 ft, 358,000 cfm, 63 lb/min loading, 917 ft/sec allowable velocity, 2.0 sec residence time, 170 gal per min, carbon steel.	86	(a)	4.37		376
2	Venturi Scrubber, 1500 gpm, 240,000 cfm, 55 lb/min loading, carbon steel, 31.5 in. WG pressure drop, 1600 hp.	128	4383 4390 4391	2.40		307
3	Cyclonic Clarifier, 1500 gpm, 55 lb/min loading, carbon steel.	5	4383	3.60		18
4	Vacuum Filter, 1500 gpm, 35 ft^2, carbon steel, 35 hp.	18	4383	3.22		58
				Capital Subtotal		759
				Indirects (@ 15%)		114
				Contingency (@ 20%)		152
				Total Capital (as of January 1971)		1,025

(a) See footnote 23.

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Operating Cost ($ /heat)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.40	1.60		2.00
2	16.63	0.25		16.88
3	–	0.25		0.25
4	0.36	0.66		1.02
Subtotal				20.15
Water(21) (1500 gpm, 90% recycle)				0.36
Disposal(22) (2 tonsper heat, Fe_2O_3, CaF_2)				1.00
Total Operating Cost				21.51

Total Operating Cost ($/heat)	21.51
Taxes and Insurance (2%, 330 days)	5.18
Capital (7.1%, 330 working days)	14.49
Pollution Control Cost ($/heat)	41.18
Pollution Control Cost ($/ton)	0.21

Table 3-35. Electric-Arc Steelmaking(26) - Estimated Economics of Control Process A Basis - Furnace Capacity of 75 Tons/Heat (4 Heats Per Day)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Water-Cooled Duct, 12,000 ft^2, t_{in} = 1000°F, t_{out} = 250°F, carbon steel, 5 in. WG pressure drop, 151,000 cfm, 160 hp.	78	4383	1.80		140
2	Baghouse, fabric filter-shaker, 73,000 cfm, 250°F, 2.5 in. WG pressure drop, 38 hp.	44	4387 4383	4.13		182
				Capital Subtotal		322
				Indirects (@ 15%)		48
				Contingency (@ 20%)		64
				Total Capital (as of January 1971)		434

All control economics footnotes are located in Section3.1.1 pages 3-10 and 3-11

Operating Cost ($ /heat)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	4.98	0.92		5.90
2	1.19	11.37		12.56
Subtotal				18.46
Water(21)	(17 gal/min)			0.12
Disposal(22)	(0.62 tons CaF_2 and Fe_2O_3/heat)			0.31
Total Operating Cost				18.89

Total Operating Cost ($/heat)	18.89
Taxes and Insurance (2%, 330 days)	6.58
Capital (7.1%, 330 working days)	18.40
Pollution Control Cost ($/heat)	43.87
Pollution Control Cost ($/ton)	0.58

Table 3-3-36. Electric-Arc Steelmaking(26) - Estimated Economics of Control Process B Basis - Furnace Capacity of 75 Tons/Heat (4 Heats Per Day)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Water-Cooled Duct, 12,000 ft^2 t_{in} = 1000°F, t_{out} = 250°F, carbon steel, 5 in. WG pressure drop, 151,000 cfm, 160 hp.	78	4383	1.80		140
2	Venturi Scrubber, 73,000 cfm, 250°F, 31.5 in. WG pressure drop, carbon steel, 485 hp.	53	4383 4390 4391	2.40		127
3	Cyclonic Separator, 620 gpm, 3.44 lb/min loading, carbon steel.	3	4383	4.00		12
4	Thickener, 620 gpm, 3.44 lb/min loading, carbon steel, 12,000 gal capacity.	10	4392	3.50		35
5	Vacuum Filter, 30 ft^2, 3.44 lb/min loading, carbon steel, 12 hp.	16	4383 4392	3.19		51
				Capital Subtotal		365
				Indirects (@ 15%)		55
				Contingency (@ 20%)		73
				Total Capital (as of January 1971)		493

Operating Cost ($ /heat)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	4.98	0.92		5.90
2	15.17	0.78		15.95
3	—	0.78		0.78
4	—	0.38		0.38
5	0.38	1.97		2.35
Subtotal				25.36
Water(21)	(670 gpm, 90% recycle)			0.48
Disposal(22)	(0.6 tons CaF_2 and Fe_2O_3/heat)			0.30
Total Operating Cost				26.14

Total Operating Cost ($/heat)	26.14
Taxes and Insurance (2%, 330 days)	4.97
Capital (7.1%, 330 working days)	13.94
Pollution Control Cost ($/heat)	45.05
Pollution Control Cost ($/ton)	0.60

All control economics footnotes are located in Section 3.1.1 pages 3-10 and 3-11

Table 3-37. Electric-Arc Steelmaking(26) - Estimated Economics of Control Process C
Basis - Furnace Capacity of 75 Tons/Heat (4 Heats Per Day)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	Spark Box, 151,000 cfm, 1000°F, assume 150,000 volts and 0.1 amp, 80 ft/sec, 16' x 16' x 12', carbon steel.	15	4383	3.0		45
2	Water-Cooled Duct, 8100 ft^2, t_{in} = 1000°F, t_{out} = 500°F, carbon steel, 150,000 cfm, 3 in. WG pressure drop, 95 hp.	53	4383	1.80		95
3	Electrostatic Precipitator, 0.9 in. WG pressure drop, 99,000 cfm, carbon steel	99	(a)	1.69		167
				Capital Subtotal		307
				Indirects (@ 15%)		46
				Contingency (@ 20%)		61
				Total Capital (as of January 1971)		414

(a) See footnote 20.

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11

Operating Cost ($ / heat)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.63	0.78		1.41
2	2.97	0.61		3.58
3	1.66	2.27		3.93
Subtotal				8.92
Water(21) (20 gpm)				0.10
Disposal(22) (0.6 tons Fe_2O_3 and CaF_2/ton)				0.30
Total Operating Cost				9.32

Total Operating Cost ($/heat)	9.32
Taxes and Insurance (2%, 330 days)	6.27
Capital (7.1%, 330 working days)	17.56
Pollution Control Cost ($/heat)	33.15
Pollution Control Cost ($/ton)	0.44

3.4 COAL COMBUSTION - ELECTRICAL POWER GENERATION

3.4.1 General

Coal is known to contain low concentrations of combined fluorine, generally present as calcium fluoride. The concentrations vary widely with an average of 0.01 weight percent for samples from diverse sources.(4302) Because of the enormous quantity of coal consumed annually (421 million tons in 1970), the quantity of fluoride potentially available for emission to the atmosphere is very large. Most of the coal sold in the country is burned; of the total, the electrical utility industry burns about 60%. Unfortunately, both number and representative character of the experimental determinations of fluoride content of gaseous and solid coal combustion products are extremely limited. To circumvent the paucity of data, the thermochemical approach discussed in Section 3.1.2 was used, in conjunction with the limited information available, to estimate the quantities and types of fluorides evolved. Coal burning for power, based on this approach, emits large quantities of gaseous hydrogen fluoride (HF) in low concentrations, in the power plant stack gas.

For purposes of simplicity, the major industry involving coal burning, electric power generation by public utilities, has been selected for analysis. The other coal-burning processes are virtually identical in effluent characteristics; they have not been included in overall emission calculations, because of uncertainties in consumption data.

3.4.2 Industry Description

Steam-electric utility plants in the United States consumed coal oil and gas equivalent to 518 million tons of coal during 1969 for the generation of electric power. Of this total, the utilities burned bituminous coal, lignite, and anthracite equivalent to more than 320 million tons total.(4283) Bituminous coal use was over 98% of the total.

3.4.3 Production Trends

Since the turn of the century, the demand for coal in the U.S. has fluctuated between 300 and 620 million tons. The low point occurred in the early years of the depression, and the peak was in World War II, with an all-time high of 620 million. Over the past 65 years, sales to large traditional customers - the railroads and space heating - have either disappeared or have become greatly reduced. Electric utilities are now coal's largest customers. In 1965, they accounted for 243 million tons, or 53% of total coal demand; in 1955, by contrast, they took 33%. In the early 1960's, this rapid increase in electric utility consumption reversed the industry's 15-year downward trend from the postwar peaks.(4281)

Total demand for U.S. coal will amount to between 1060 million tons and 1300 million tons by the year 2000.(4281,4282) Annual growth will range between 2.4% and 4.0%, as opposed to a rate of about 5% for the past 10 years.(4281,4282)

Electric utilities will consume between 780 million and 1080 million tons in the year 2000, accounting for most of the domestic use.(4281,4282,4283) Because of competition from nuclear power, coal's rate of growth in this market will decrease to between 3.4% and 4.0%, compared to 5.6% over the last 10 years. Table 3-38 presents a summary of data found in literaure and obtained from private sources.

Since the first nuclear plant went into operation in 1957 at Shippingport, Pennsylvania, nuclear power has risen rapidly. In some cases, the choice of nuclear power was made strictly on the basis of cost, but increasingly stringent regulations on air, water, and land pollution have influenced a decision not to use coal. Under these circumstances and because of favorable costs, electric utilities have moved to nuclear power. An example is the recent selection of nuclear over coal in one of the latter's traditional strongholds, the TVA region, where coal costs to the system are the lowest of any utility in the nation. Such competition, spurred also by air pollution factors, will increase; and, as a result, coal's share of the electric generation market will drop from its current

Table 3-38. Coal Usage

	1965 (millions of tons)	1970 (millions of tons)	1980 (millions of tons)	Expected Growth Rate (Percent)	Extrapolated to Year 2000 (millions of tons)
Total coal usage	459(4281)	421(4281)	660(4281)	2.4	1060
				4.0	1300
Electrical utility coal usage			400(4281)	3.4(4281)	780
		320(4282)		3.9	1000(4282)
		333*(4283)		3.0(4283)	1080*

*Values used in this study.

level of 54 to 37% in 1980.(4284) However, because of the overall growth in power generation, the volume of coal used by utilities will increase substantially, as noted above.

3.4.4 Control Techniques

Currently, with only four known exceptions in this country, coal burning power plant pollution control equipment is limited to fly ash abatement. The exceptions are facilities using alkaline injection and/or wet scrubbing systems, including the limestone injection-wet scrubbing processes currently under investigation by the Office of Air Programs for abatement of SO_2 generated by coal burning steam-electric plants. These processes should also remove substantial portions of the HF content of the flue gases. In theory, due to the high solubility of HF in water and the extreme insolubility of CaF_2, HF should be absorbed very rapidly by the wet scrubber solutions. Practically, the actual effectiveness of fluoride emission control via the limestone injection-wet scrubbing processes will require experimental verification because of the relatively low concentrations of hydrogen fluoride in the flue gases. These concentrations are of the order of 20 to 100 parts per million (volume).

Coal contains minor quantitites of inorganic fluorides, with a nominal concentration of approximately 0.01 weight percent fluorine.(4302) (This value is considerably lower than the 400 ppm value reported as maximum from another source.)(4285) At the temperatures associated with combustion, near complete volatilization and conversion to HF of the fluoride content is probable; however, a portion of the evolved fluoride may adsorb or react with fly ash or other solid surfaces in cooler parts of the process. A recent study by Orning, et al,(4231) indicates the following distribution of fluoride from coal combustion:

Retention in ash overhead	10%
Exit as gas	70%
Unaccounted	20%
	100%

TRW-RRI data files indicate that about 10% of the fluoride contained in the coal fed to the burner is removed with the fly ash in the precipitator while 80% is emitted to the atmosphere in the gas phase as HF; the remaining 10% is emitted as suspensoid particulate (micron size uncollected fly ash).

Thermochemical analyses of the coal/air system were performed using a proprietary chemical analysis program assuming 20% excess air in the combustion process. Calculations were performed at one atmosphere total pressure and at temperatures ranging from the adiabatic flame temperature (approximately 4000°F under these conditions) to below 1300°F, the probable lower limit for gaseous phase attainment of species equilibrium at finite rates. The results of these calculations are presented in Figure 3-28, which indicates the percent conversion to HF (gaseous) at equilibrium of the fluoride species contained in coal as a function of temperature.*

At high temperatures (above 2000°F), HF (g) is almost the sole equilibrium species containing fluorine and the time required for attainment of equilibrium is virtually microseconds. As temperatures decrease, the rate of attainment of equilibrium via gas phase reaction decreases exponentially. Thus, even though equilibrium conditions below 1480°F shift to favor increased formation of CaF_2, the rate of gas phase reaction plus the adsorption/chemisorption process rates is so low that overall reversion to CaF_2 of the HF formed at higher temperatures does not take place to an extent greater than 20% in the time available in the power plant. It should be noted that a probable major mechanism for reversion to CaF_2 at the lower temperatures (below 1300°F) is the absorption/chemisorption process that involves reaction between the suspensoid solid CaO of the fly ash and gaseous HF.

A soluble fluoride emission factor of 0.16 lb F/ton coal burned was used for the emission determinations. The current and future estimations of soluble fluoride (reflecting no soluble fluoride abatement) emissions

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*The percent conversion is almost independent of CaF_2 content for bituminous coals, in the range of 0.005 to 0.100% (wt).

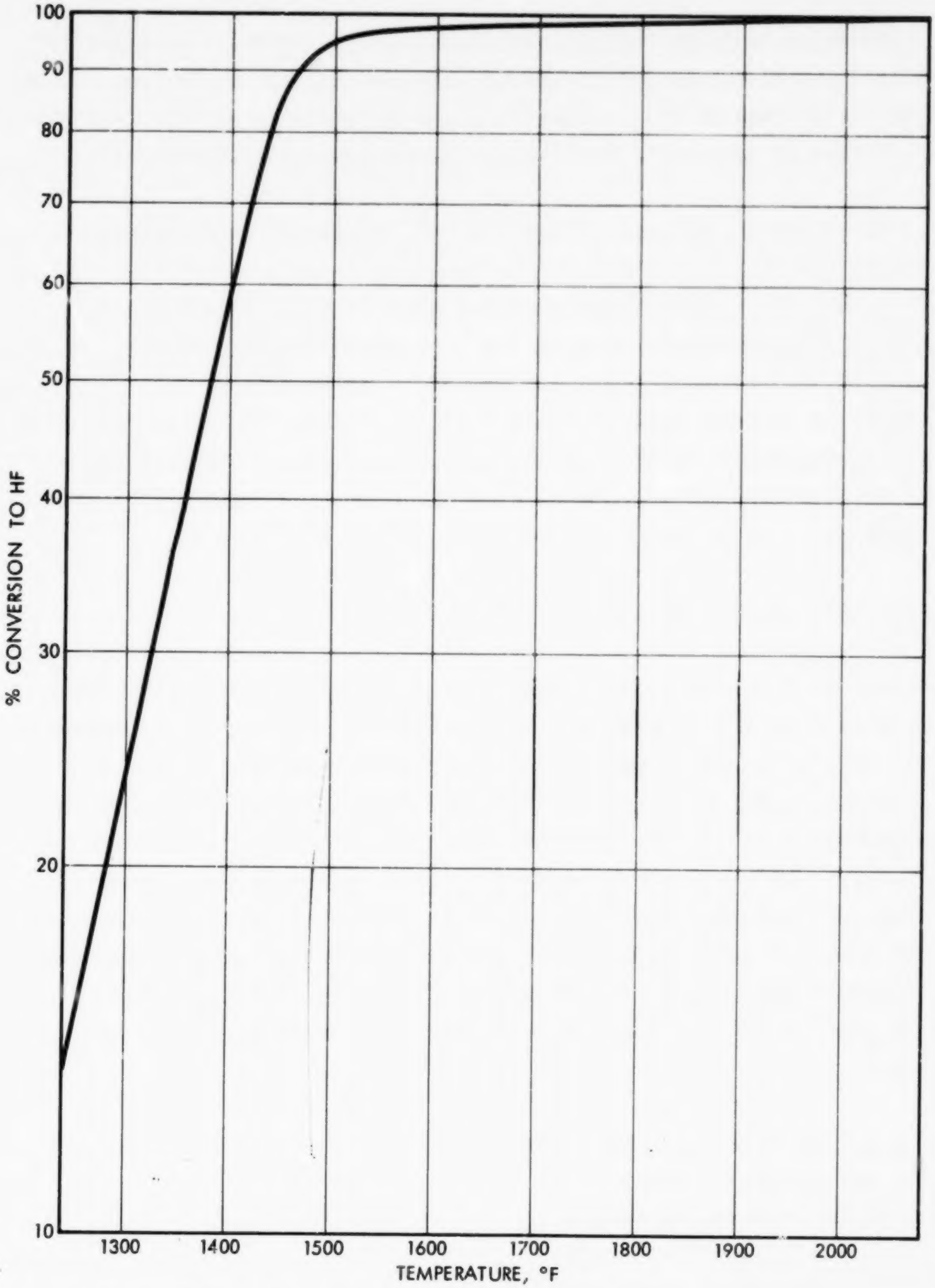


Figure 3-28. Percent Conversion of Fluorine Species in Coal to HF at Equilibrium

are 26,600 tons (as F) in 1970 and 86,400 tons (as F) in 2000. If 99% fluoride control is applied, the emission level will drop to 860 tons (as F) in 2000.

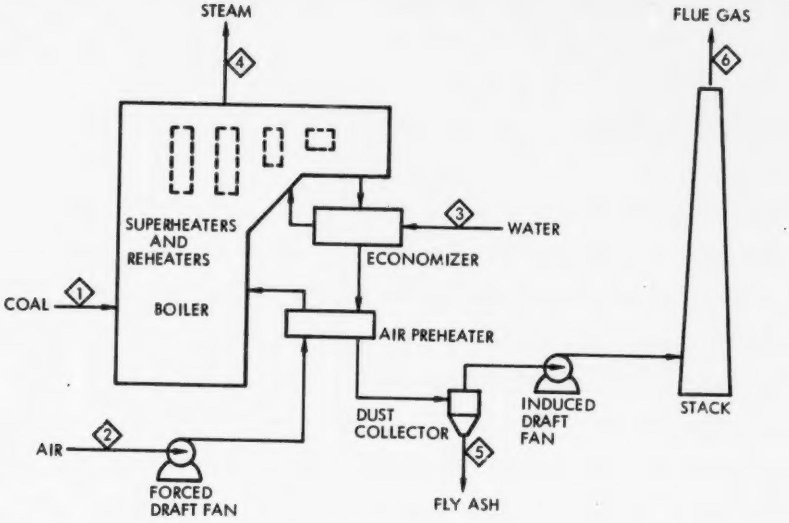
3.4.5 Process Description

Most coal burning power plants air inject pulverized coal (ground to 90% through 200 mesh) through special burners into a combustion chamber. As indicated by the process flow diagram in Figure 3-29, the combustion chamber has a formed draft feed of secondary air. All of the burning is completed in the combustion chamber at flame temperatures over 4000°F for a 20% excess of air. Reaction between the metallic fluorides contained in the coal and the hydrogen from water or other sources is almost quantitative and instantaneous at this temperature. Hydrogen fluoride evolution takes place almost completely in the combustion chamber.

From the combustion chamber, the hot gas and suspensoid fly ash flow to the boiler, where heat exchange takes place in the water jacket boiler tubes, generating steam and dropping the gas temperature to levels where adsorption or reaction of the evolved HF by the fly ash starts. After further temperature reduction in the superheaters, reheaters and air preheaters, the combustion gas stream ("flue gas") is stripped of the major portion of the suspensoid fly ash in the dust collectors and is discharged through the stack to the atmosphere.

All currently operating coal burning electric utility plants use dust collection devices for removal of fly ash. With only four known exceptions, the dust collection devices are dry systems, which remove only particulate material from the flue gas. Gaseous pollutants, other than the small amounts removed by adsorption or reaction with the particulate material, pass through dry collection systems unhindered and uncontrolled.

The process flow diagram and mass balances presented in Figure 3-29 give data for a typical power plant burning coal of average fluoride content.


STEAM
4
FLUE GAS
6
SUPERHEATERS AND REHEATERS
3
WATER
ECONOMIZER
COAL
1
BOILER
AIR PREHEATER
INDUCED DRAFT FAN
STACK
DUST COLLECTOR
AIR
2
5
FORCED DRAFT FAN
FLY ASH

BASIS: 1100 MW POWER PLANT

PROCESS STREAMS - TONS/DAY

Material	Stream Number					
	1	2	3	4	5	6*
HF (Equiv.)						1.17(g)(b)
CaF_2	2.85(s)(b)				0.29(s)(b)	0.29(s)(b)
Total Fluorides	2.85				0.29	1.46
Total as F	1.39				0.14	1.25
Coal	13,900(s)(a)					
N_2		97,000(l)(Est)	80,000(g)	80,000(g)		97,000(g)(a)
O_2		25,800(g)(Est)				2,700(g)(a)
H_2O		800(g)(Est)	(Est)	(Est)		6,000(g)(a)
CO_2						29,000(g)(a)
SO_2						800(g)(a)
NO_X						50(g)(a)
Fly Ash					850(s)(Est)	200(s)(Est)
Approximate Total Stream	13,900	123,600	80,000(c)	80,000	850	136,700

*Gaseous Effluent Stream
Soluble Fluoride Evolution Factor = 0.16 lbF/ton coal
Soluble Fluoride Emission Factor = 0.16 lbF/ton coal

(a) Ref. 4384
(b) Ref. 4266
(c) Includes makeup water for boiler blow down

Figure 3-29. Coal-Fired Plant (1100 mw) - Uncontrolled Process Model

3.4.6 Economic Analysis

3.4.6.1 Basic Process

The economics estimated for coal fired power plants are summarized in Table 3-39 as a basis for future use in determining the economic impact of control of soluble fluoride emissions.

3.4.6.2 Impact of Controls

The absence of any current, clearly defined techniques for controlling fluoride emissions from coal burning power plants prevents attempting an economic analysis of control costs.

Table 3-39. Estimated Economics of Coal Firing Power Plants (Excluding Pollution Control Cost)

	CAPACITY		
	100 mw	400 mw	700 mw
Installed Capital[1] Cost	31.5 $MM	74.0 $MM	125.4 $MM
Operating Costs[2]			
Direct Costs			
Coal (9000 Btu/kw hr at 22.3¢/MM Btu FOB Mine)	2.01 mills/kwh	2.01 mills/kwh	2.01 mills/kwh
Coal Transportation (4.7¢/MM Btu)	0.42	0.42	0.42
Operation and Maintenance[3]	0.49	0.44	0.43
Total Direct Costs	2.92	2.87	2.86
Indirect Costs			
Depreciation (3 1/3% per year)	1.71	1.01	0.97
Interest Charges (7% of ave debt at debt/equity of 0.5)	0.90	0.53	0.15
Insurance (0.2% of capital)	0.10	0.06	0.06
Local Taxes (1.2% of capital)	0.60	0.36	0.35
Total Indirect Costs	3.31	1.96	1.89
Total Cost (mills/kwh)	6.23 mills/kwh	4.83 mills/kwh	4.75 mills/kwh
Total Annual Cost ($MM/yr)	3.82 $MM/yr	11.85 $MM/yr	20.39 $MM/yr
Product Revenue ($MM/yr; based on a 7% return on investment)	7.34	20.13	34.43
Profit After Taxes (at 50%; $MM/yr)	1.76	4.14	7.02
Cash Flow ($MM/yr)	2.81 $MM/yr	6.61 $MM/yr	11.20 $MM/yr
Return on Investment	7%	7%	7%

(1) Includes transmission capital cost from generator to distribution area

(2) Based on a net plant factor of 70%

(3) Primarily labor for plant and transmission

(4) Equity plus debt estimated at 1.3 x capital less depreciation for return on investment calculation.

3.5 PHOSPHATE ROCK PROCESSING

3.5.1 General

Phosphate rock, which is predominantly insoluble fluorapatite [$3Ca_3(PO_4)_2 \cdot CaF_2$] and hydroxyapatite [$3Ca_3(PO_4)_2 \cdot Ca(OH)_2$], is the raw material from which the water and citrate* soluble phosphates and polyphosphates sold to the ultimate consumer are made. Each of the end products requires thermal and/or chemical processing of the phosphate rock as an early process step, with concomitant release and partial evolution of the fluoride content of the rock as gaseous, soluble fluorides—silicon tetrafluoride (SiF_4) and/or hydrogen fluoride (HF). Many of the intermediate and final process steps necessary for obtaining saleable commodities cause additional evolution of SiF_4 and/or HF.

3.5.2 Industry Description

The following subsections will cover only the fluoride evolving manufacturing processes for obtaining saleable commodities from phosphate rock. These are the manufacture of wet process phosphoric acid; diammonium phosphate; triple superphosphate; normal superphosphate; electrothermal process phosphorus; and defluorinated phosphate rock.

One gauge of the magnitude of the problem handled by the phosphate industries is the volume of rock produced and processed, viewed in the context of a fluoride content which ranges from 3 to 4 weight percent (nominal = 3.5%). Tables 3-40, 3-41, and 3-42 present production and usage distribution for 1969 for phosphate rock mined in the United States. The figures given are those of the Bureau of Mines, adjusted to include only direct usage of rock for triple superphosphate manufacture, and to reflect all rock used for wet-process phosphoric acid manufacture.

The state of the art of control technology in the phosphate rock processing industry is quite good. Systems for fluoride emission control have been in service in the phosphate industry for many years. Concentration

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*Solubility in neutral ammonium citrate solution is used as the means of measuring availability as nutrient of the P_2O_5 content of processed phosphates. All water soluble phosphates are citrate-soluble; only a part of the citrate soluble phosphates are also water soluble.

Table 3-40. Production of Phosphate Rock in the United States (4262) (Thousand Short Tons)

	Florida[1]		Tennessee[2]		Western States		Total United States[3]	
Use	Rock	P_2O_5 Content	Rock	P_2O_5 Content	Rock	P_2O_5 Content	Rock	P_2O_5 Content
Domestic:								
Agricultural	17,501	5,629	-----	---	1,039	328	18,540	5,958
Industrial	553	166	3,193	851	3,107	772	6,853	1,789
Total	18,054	5,795	3,193	851	4,146	1,100	25,393	7,747
Exports	10,811	3,519	-----	---	525	166	11,336	3,685
Total	28,865	9,313	3,193	851	4,672	1,266	36,730	11,431

[1] Includes North Carolina

[2] Includes Alabama (1969)

[3] Data may not add to totals shown because of independent rounding

Table 3-41. Phosphate Rock Sold or Used by Producers, by Uses and States (4262) in 1969 (Thousand Short Tons)

	Mine Production		Mine Production Used Directly		Washer Production		Marketable Production	
State	Rock	P_2O_5 Content	Rock	P_2O_5 Content	Rock	P_2O_5 Content	Rock	P_2O_5 Content
1969								
Florida[1]	111,178	15,711	92	28	29,838	9,575	29,930	9,603
Tennessee[4]	5,648	1,080	533	128	2,741	730	3,274	858
Western States[2]	4,886	1,253	3,539	905	982	318	4,521	1,223
Total[3]	121,712	18,044	4,164	1,061	33,561	10,623	37,725	11,684

[1] Includes North Carolina

[2] Includes California, Idaho, Montana, Utah, and Wyoming

[3] Data may not add to totals shown because of independent rounding

[4] Includes Alabama

Table 3-42. Direct Uses of Phosphate Rock in the United States in 1969 (Thousands of Short Tons)

Use	Rock	P_2O_5 Equivalent
Wet Process Phosphoric Acid	12,688	4028
Electric Furnace Phosphorus	6,758	1759
Triple Superphosphate	1,085	374
Normal Superphosphate	3,524	1150
Other	1,338	436
	25,393	7747

of phosphate rock processing plants in particular geographical areas such as Florida has led to increased surveillance by environmental control authorities. This is due both to concern for the environment and to the legal actions brought by plant neighbors due to alleged damages to cattle, plants, or fruit because of the effects of fluoride emissions. This attention has caused the companies concerned to institute effective monitoring and control of fluoride emissions at many of the phosphate processing plants. In this context, control means prevention of emission of fluorides into the ambient environment. While it is true that fluorine and fluorine compounds are valuable industrial commodities and that the fluorine liberated from phosphate rock processing annually could constitute a major supply of fluorine, fluoride released from processing of rock is considered by the industry a waste product to be disposed of in the most expeditious manner. Emphasis on more restrictive and expensive fluoride control requirements as well as an increased focus on the value of the waste fluoride is adding emphasis to efforts to capture the emitted fluorides in a saleable form.

3.5.3 Production Trends

The principal solid fertilizer products in the future will continue to be ammonium phosphates, triple superphosphates, normal superphosphates, solid and liquid NPK mixtures, and nitrophosphates. Phosphoric acid will continue to be the key intermediate in the production of triple superphosphate, the ammonium phosphates and superphosphoric acid, and will be used as now in mixtures and direct applications. It is doubtful that any new product will appear within the next thirty years that is not related to one or another of these materials or that will be independent of the use of phosphoric acid, sulfuric acid or nitric acid as an intermediate.(4288) Estimated future production levels in the United States of the primary phosphate containing materials are listed in Tables 3-43, 3-44, and 3-45.

These projections reflect an outlook for a continually declining market for normal phosphate and a stable market attended by some increase for triple superphosphate; the market for ammonium phosphate is expected to expand rapidly until 1980 and then drop down somewhat by 2000. Superphosphoric acid, which is now a main supplier to the liquid market, will increase its share continually for the foreseeable future. Merchant phosphoric and superphosphoric acids are expected to account for about 25% of the P_2O_5 liquid fertilizer by the year 2000. Nitrophosphates appear to have a long term outlook for slow growth.

Table 3-43. U.S. Agricultural Phosphate - Recent and Estimated Future Production(4226) (all tonnages as P_2O_5)

					Estimated					
	1950		1960		1970		1980		2000	
	MM Tons	% Mkt.	MM Tons	% Mkt.	MM Tons	% Mkt.	MM Tons	% Mkt.	MM Tons	% Mkt.
Normal Superphosphate	1.7	85.0	1.3	46.4	0.7	13.5	0.3	4.1	0.2	1.5
Triple Superphosphate	0.3	15.0	1.0	35.7	1.4	26.9	1.5	20.2	2.7	19.5
Ammonium Phosphates	-	-	0.4	14.3	2.4	46.1	4.3	58.1	7.0	50.7
Superphosphoric Acid	-	-	-	-	0.4	7.6	0.8	10.8	2.8	20.3
Merchant Phosphoric Acid (mixtures, direct application and animal feed phosphate)	-	-	0.1	3.6	0.2	3.8	0.3	4.1	0.7	5.1
Nitrophosphates	-	-	-	-	0.1	1.9	0.2	2.7	0.4	2.9
Total Agricultural P_2O_5 Production	2.0	100.0	2.8	100.0	5.2	100.0	7.4	100.0	13.8	100.0
Total Agricultural P_2O_5 Consumption	2.0		2.6		4.6		7.2		13.7	
Total Wet Process H_3PO_4	-	-	-	-	3.8	-	-	-	13.1	-

Table 3-44. Defluorination of Phosphate Rock

	1970	2000
Phosphate Rock Used (1000 tons as P_2O_5)	87.7(4264)	141.2
U.S. Population (Millions)	208.8	336.2
Per-Capita Consumption (lb/person)	0.84	0.84

Table 3-45. Electric Furnace Phosphorus Production

	1968	2000
Phosphate Rock Used (1000 tons as P_2O_5)	1570(4393)	2620
U.S. Population (millions)	202.3	336.2
Per-Capita Consumption (lb/person)	15.56	15.56

Table 3-46. Phosphate Industries Fluoride Emissions

	Wet Process Phosphoric Acid	Diammonium Phosphate	Triple Superphosphate	Normal Superphosphate	Electrothermal Phosphorus	Defluorination of Phosphate Rock	Industry Totals
1970 Production (10^6 tons/yr)	3.8$^{(B)}$	2.4$^{(B)}$	1.4$^{(B)}$	0.7$^{(B)}$	1.6$^{(A,D)}$	0.09$^{(A,)}$	10.4$^{(B)}$
Projected 2000 Production (10^6 tons/yr)	13$^{(B)}$	7.0$^{(B)}$	2.7$^{(B)}$	0.2$^{(B)}$	2.6$^{(A)}$	0.14$^{(A)}$	26.3$^{(B)}$
Soluble Fluoride Evolution Factor	4.07$^{(C)}$ lb F/ton P_2O_5 in Product	1.31$^{(C)}$ lb F/ton P_2O_5 in Product	21.2$^{(C)}$ lb F/ton P_2O_5 in Product	71 lb F/ton P_2O_5 in Product	30 lb F/ton P_2O_5 In Phosphate Rock Feed	243$^{(C)}$ lb F/ton P_2O_5 in Phosphate Rock Feed	16 to 9.3$^{(C,E)}$ lb F/ton P_2O_5 Equiv. in Products
Soluble Fluoride Emission Factor with Current Control	3.36$^{(C)}$ lb F/ton P_2O_5 in Product	0.23$^{(C)}$ lb F/ton P_2O_5 in Product	5.4$^{(C)}$ lb F/ton P_2O_5 in Product	14.2 lb F/ton P_2O_5 in Product	5.1 lb F/ton P_2O_5 in Phosphate Rock Feed	39$^{(C)}$ lb F/ton P_2O_5 Phosphate Rock Feed	4.1 to 3.1$^{(C,F)}$ lb F/ton P_2O_5 Equiv. in Products
Soluble Fluoride Emission Factor with 99% Control	0.04$^{(C)}$ lb F/ton P_2O_5 in Product	0.013$^{(C)}$ lb F/ton P_2O_5 in Product	0.21$^{(C)}$ lb F/ton P_2O_5 in Product	0.71 lb F/ton P_2O_5 in Product	0.30 lb F/ton P_2O_5 in Phosphate Rock Feed	2.4 lb F/ton P_2O_5 in Phosphate Rock Feed	0.09$^{(C)}$ lb F/ton P_2O_5 Equiv. in Products
Soluble Fluoride Evolved in 1970 (10^3 Tons F/year)	7.73$^{(C)}$	1.57	14.8	24.9	24.0	10.9	83.9
Soluble Fluoride Evolved in 2000 (10^3 tons/year)	26.4$^{(C)}$	4.59	28.6	7.10	39.0	17.0	123
Soluble Fluoride Emission in 1970 (10^3 tons F/year)	6.38$^{(C)}$	0.28$^{(C)}$	3.78$^{(C)}$	4.97	4.08	1.76$^{(C)}$	21.3
Soluble Fluoride Emission in 2000 with Current Control (10^3 tons F/year)	21.8$^{(C)}$	0.81$^{(C)}$	7.29$^{(C)}$	1.42	6.63	2.73$^{(C)}$	40.7
Soluble Fluoride Emission in 2000 with 99% Control (10^3 tons F/year)	0.26$^{(C)}$	0.046$^{(C)}$	0.28$^{(C)}$	0.071	0.39	0.17$^{(C)}$	1.22

(A) Expressed as P_2O_5 equivalent in phosphate rock feed

(B) Expressed as P_2O_5 equivalent in product

(C) Includes gypsum pond emissions

(D) 1968 Data

(E) Reflects change due to shifts in production trends thru 2000

3.5.4 Fluoride Control and Emissions Summary

Fluoride control systems for the phosphate rock processing industry typically utilize water scrubbers to absorb the gaseous fluoride effluents from the individual processes. The individual control systems appropriate for each fertilizer product are described in the following section.

Soluble fluoride evolution and emission associated with the current and projected production levels are tabulated in Table 3-46. It should be noted that the emission factors of the individual processes have been allocated their share of the soluble fluorides volatilized from gypsum ponds so that each emission factor is a composite of appropriate manufacturing process emissions and gypsum pond emissions.

3.5.5 Process Description

3.5.5.1 Wet Process Phosphoric Acid

Process Description. Wet process phosphoric acid is produced by the digestion of phosphate rock with sulfuric acid. The wet process acid contains impurities that preclude its use in pharmaceuticals and similar products so that acid made from elemental phosphorus (furnace grade or "white acid") is used for these products. Wet process acid is used almost exclusively in the manufacture of concentrated phosphate fertilizers. The reactants in wet process phosphoric acid manufacture are phosphate rock, which contains 30 to 35% P_2O_5 and 3 to 4% fluoride, and sulfuric acid at 93 to 99% concentration. The primary products of the reaction are impure, dilute, phosphoric acid containing 28 to 32% P_2O_5 and impure gypsum (calcium sulfate dihydrate).

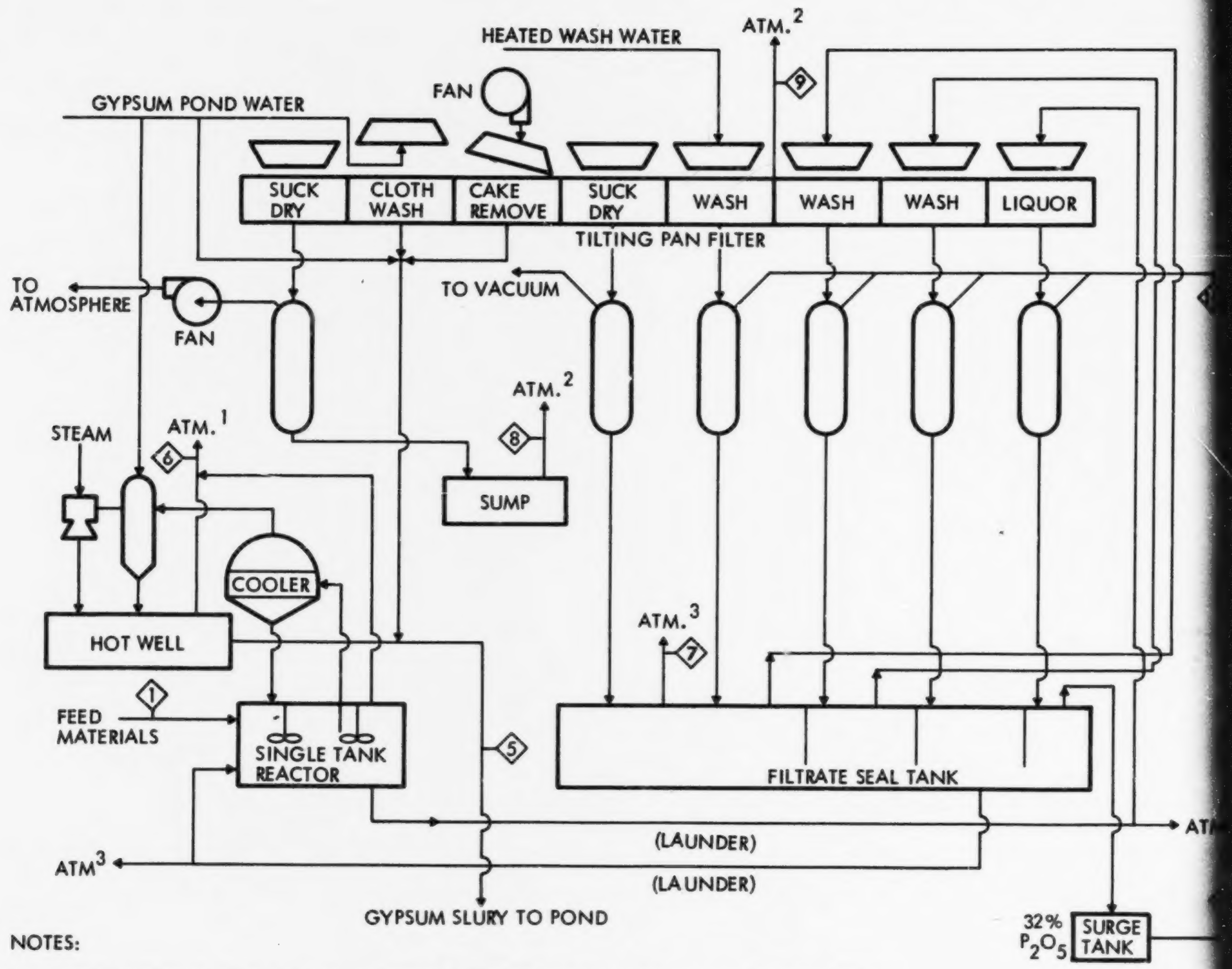
Various concentrations of wet process phosphoric acid are used for the different fertilizer products. Although some dilute (roughly 32% P_2O_5) acid is used directly for manufacture of a few products and acid concentrated to approximately 38 to 40% is used for some of the ammonium phosphates, the great majority of the acid produced is concentrated to about 54% P_2O_5.

Essentially the same basic processing steps are involved in making wet process phosphoric acid at any acid manufacturing facility although the process hardware and flow sheet will vary from plant to plant. A typical modern wet process phosphoric acid plant flow sheet is shown in Figure 3-30. Individual plants differ in the number and arrangement of reactors, recycle flows, types of evaporators, etc. The similarity of requirements at all plants has caused a few given hardware items to become "the accepted devices" for given applications. For instance, most modern plants now use tilting pan filters for gypsum filtration. This phenomenon leads to some measure of uniformity in equipment selection, plant size, and emission factors for wet acid plants.

Production Trends. As shown in Table 3-46, production of wet process phosphoric acid is more than twice the production of the next largest phosphate rock product. The major uses of the acids are in the production of ammonium phosphates, triple superphosphate, and dicalcium phosphate with about 75 percent of production going into ammonium phosphates and about 20% into triple superphosphate. Concentration of the acid to produce superphosphoric acid (approximately 70% P_2O_5 content) has promise of becoming increasingly significant. Superphosphoric acid is a concentrated, convenient form of P_2O_5 for shipping or further processing.

The production of wet process phosphoric acid is expected to grow from 3.8 million tons per year in 1970 (as P_2O_5) to 13 million tons per year in 2000.(4226)

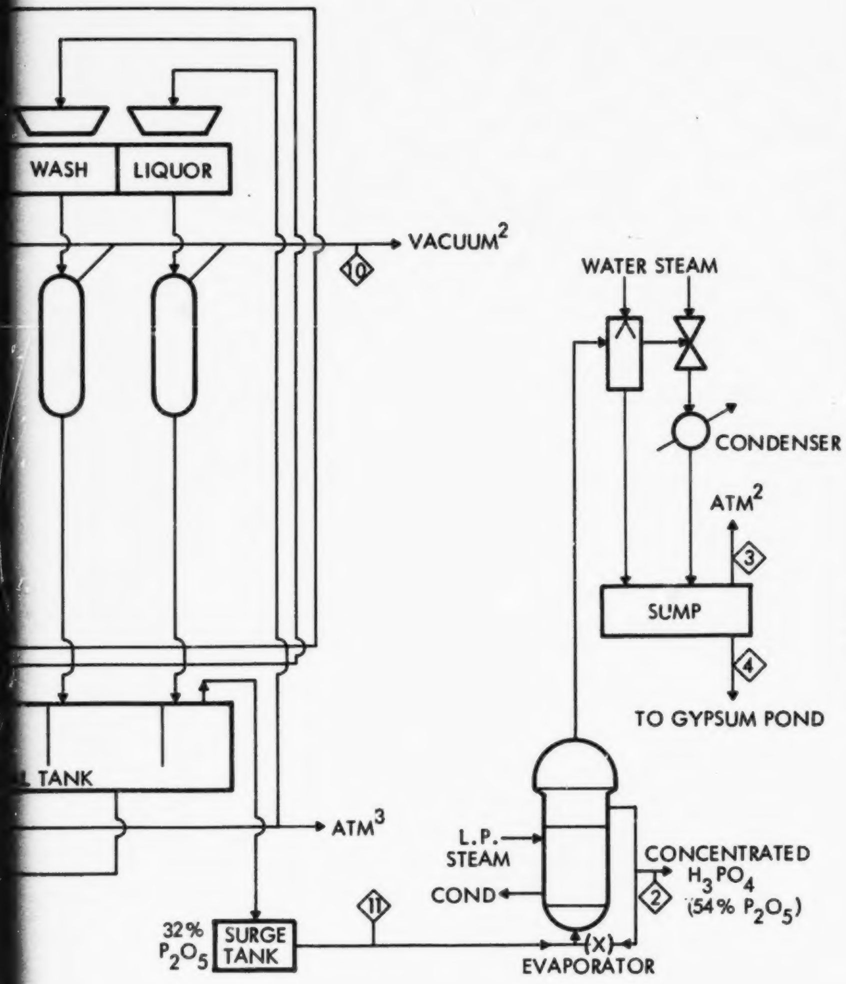
Fluoride Emission Control Techniques. Standard practice in emission control from wet process phosphoric acid plants involves the universal application of wet scrubbing systems. Specific types of wet scrubbing systems currently employed include the liquid ejector venturi scrubber, liquid impingement control systems, and the spray tower. These processes are presented as control process flow diagrams and mass balances in Figure 3-31.


HEATED WASH WATER
ATM. 2
9
GYPSUM POND WATER
FAN
SUCK DRY
CLOTH WASH
CAKE REMOVE
SUCK DRY
WASH
WASH
WASH
LIQUOR
TILTING PAN FILTER
TO ATMOSPHERE
FAN
TO VACUUM
ATM. 2
8
STEAM
ATM. 1
6
SUMP
COOLER
HOT WELL
ATM. 3
7
1
FEED MATERIALS
SINGLE TANK REACTOR
5
FILTRATE SEAL TANK
(LAUNDER)
ATM
ATM 3
(LAUNDER)
GYPSUM SLURY TO POND
32% P_2O_5
SURGE TANK

NOTES:

1. APPROXIMATELY 80% OF ALL GASEOUS FLUORIDE POLLUTANTS FOUND IN THIS STREAM.
2. THOSE STREAMS WILL CONTAIN SMALL AMOUNTS OF FLUORIDE POLLUTANTS AND MAY BE SCRUBBED PRIOR TO VENTING.
3. POSSIBLE FUGITIVE EMISSIONS FROM LAUNDERS (SEMICIRCULAR TROUGHS)

A


WASH
LIQUOR
VACUUM^2
10
WATER STEAM
CONDENSER
ATM^2
3
SUMP
4
TO GYPSUM POND
L TANK
ATM^3
L.P. STEAM
COND
CONCENTRATED H_3PO_4 (54% P_2O_5)
2
32% P_2O_5
SURGE TANK
11
(X)
EVAPORATOR

M.

BASIS - 1000 TONS/DAY PHOSPHORIC ACID

PROCESS STREAMS - TONS/DAY

	Stre				
Material	1	2	3**	4*	
H_2SiF_6		23(1)$^{(F)}$		44(1)(Est)	107
HF					
SiF_4			Unknown		
CaF_2 equiv.	280$^{(G)}$				4.
Total Fluorides	280	23	Unknown	44	11
Total as F	140	18		35	8
Phosphate Rock	3300				5
Sulfuric Acid (96%)	2900				
Phosphoric Acid (54%P_2O_5)		1850			
Phosphoric Acid (32%P_2O_5)					
H_2O				1270(g)(Est)	
Gypsum					50
Approx. Total Stream	6400	1900		1300$^{(A)}$	50

Notes: * Liquid streams that are possible pollutant sources

** Gaseous effluent streams

(A) Plus process water used in filtration and gypsum dil

(B) Plus approx. 15000 scfm of reactor off-gases.

(C) Plus other diluent gases.

(D) Plus 20000 scfm of dilution air.

(E) References 4262 and 2359

(F) Reference 4265

(G) Reference 4264

Soluble fluoride evolution factor = 0.93 lb F/ton P_2O_5

Soluble fluoride evolution factor = 3.14 lb F/ton P_2O_5

Soluble fluoride evolution factor = 4.17 lb F/ton P_2O_5

B

BASIS - 1000 TONS/DAY PHOSPHORIC ACID (P_2O_5) PRODUCTION

PROCESS STREAMS - TONS/DAY

Stream Number										
1	2	3**	4*	5*	6**	7**	8**	9**	10**	11
	$23(1)^{(F)}$		44(1)(Est)	107(2)(Est)						67(1)
		Unknown			$0.5(g)^{(E)}$	$0.03(g)^{(E)}$	$0.03(g)^{(E)}$	$0.01(g)^{(E)}$	$0.03(g)^{(E)}$	
$280^{(G)}$				4.2(s)(Est)	$0.2(s)^{(E)}$					
280	23	Unknown	44	111	0.7	0.03	0.03	0.01	0.03	67
140	18		35	86.5	0.4	0.02	0.02	0.007	0.02	53
3300				50(Est)	$3(s)^{(E)}$			$0.06(s)^{(E)}$		
2900										
	1850									
										3120
			1270(g)(Est)							
				5000						
6400	1900		$1300^{(A)}$	$5000^{(A)}$	$3^{(B)}$	$0.03^{(C)}$	$0.03^{(C)}$	$0.1^{(D)}$	$0.03^{(C)}$	3100

id streams that are possible pollutant sources

ous effluent streams

process water used in filtration and gypsum dilution.

approx. 15000 scfm of reactor off-gases.

other diluent gases.

20000 scfm of dilution air.

ences 4262 and 2359

ence 4265

ence 4264

luoride evolution factor = 0.93 lb F/ton P_2O_5 produced, excluding gypsum pond.

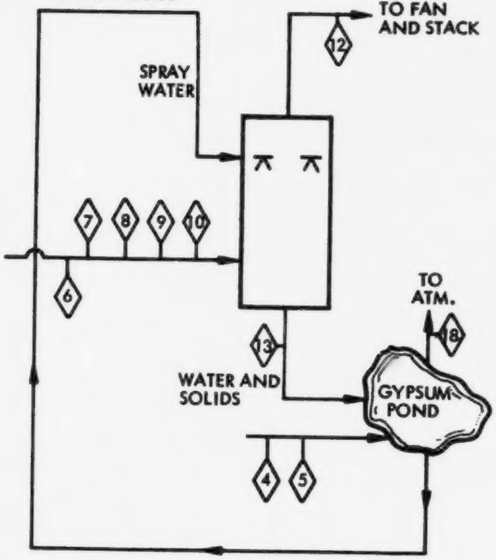
luoride evolution factor = 3.14 lb F/ton P_2O_5 produced, from gypsum pond.

luoride evolution factor = 4.17 lb F/ton P_2O_5 produced, including gypsum pond.

Figure 3-30. Wet-Process Phosphoric Acid Production — Uncontrolled Model

Ⓐ

WET SPRAY SCRUBBER
EFF. = 60% (EST.) PARTICULATE
65% GASEOUS

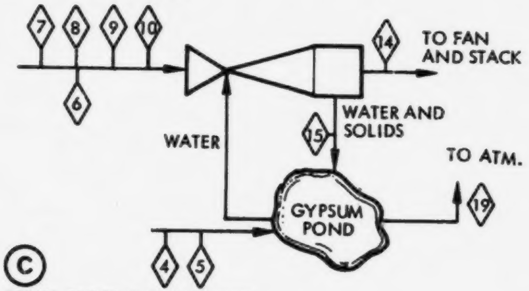

TO FAN AND STACK
12
SPRAY WATER
7
8
9
10
6
13
TO ATM.
18
WATER AND SOLIDS
GYPSUM POND
4
5

NOTE:

1. ALL OR PART OF 7 8 9 10 COMPLETELY UNCONTROLLED IN MANY PLANTS.
2. A FEW PLANTS LIME THEIR GYPSUM PONDS TO pH_4 TO DECREASE HF EVOLUTION

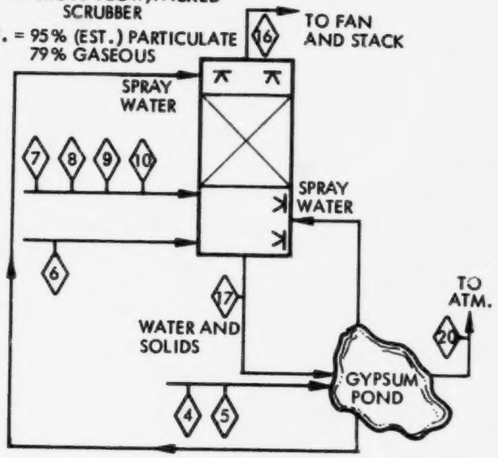
Ⓑ

VENTURI SCRUBBER
EFF. = 99% PARTICULATE
90% GASEOUS


7
8
9
10
6
14
TO FAN AND STACK
WATER
15
WATER AND SOLIDS
TO ATM.
19
GYPSUM POND
4
5

Ⓒ

SPRAY CROSS-FLOW, PACKED SCRUBBER
EFF. = 95% (EST.) PARTICULATE
79% GASEOUS


16
TO FAN AND STACK
SPRAY WATER
7
8
9
10
6
SPRAY WATER
17
WATER AND SOLIDS
TO ATM.
20
GYPSUM POND
4
5

Material	6
SiF_4	0.5(g)$^{(A)}$
HF	
CaF_2	0.2(s)$^{(A)}$
Total Fluorides	0.7
Total as F	0.4
Phosphate Rock	3(s)$^{(A)}$
Approx. Total Stream	3$^{(B)}$

* Gaseous effluent str

(A) References 4262 an
(B) Plus approx. 15,00
(C) Plus other diluent
(D) Plus 20,000 scfm o
(E) Plus 1.47 x 10^6 ga
(F) Assumes no lime ad

NOTE: Composition of
uncontrolled ma

Source
Control Device Emissio
Wet Process Phosphate Acid Gypsum Ponds
Total Soluble Fluoride Emission

Overall soluble fluor
(including gypsum pon

A

BASIS-1000 TONS/DAY PHOSPHORIC ACID (54% P_2O_5) PRODUCTION

PROCESS STREAMS - TONS/DAY

	Stream Number													
rial	6	7	8	9	10	12*	13	14*	15	16*	17	18*	19*	20*
	0.5(g)$^{(A)}$ 0.2(s)$^{(A)}$	0.03(g)$^{(A)}$	0.03(g)$^{(A)}$	0.01(g)$^{(A)}$	0.03(g)$^{(A)}$	0.21(g)$^{(A)}$ 0.08(s)$^{(A)}$	0.39(aq) 0.12(aq)	0.06(g)$^{(A)}$ 0.002(s)$^{(A)}$	0.54(aq) 0.2(aq)	0.13(g)$^{(A)}$ 0.01(s)$^{(A)}$	0.47(g) 0.19(aq)	1.65(g)$^{(A)}$	1.65(g)	1.65(g)$^{(A)}$
ides	0.7	0.03	0.03	0.01	0.03	0.29	0.51	0.062	0.74	0.14	0.66	1.65	1.65	1.65
as F	0.4	0.02	0.02	0.007	0.02	0.19	0.34	0.044	0.49	0.10	0.44	1.57	1.57	1.57
hate	3(s)$^{(A)}$			0.06(s)$^{(A)}$		1.22(s)	1.84(aq)	0.03	2.97	0.18	2.91			
x.	3$^{(B)}$	0.03$^{(C)}$	0.03$^{(C)}$	0.1$^{(D)}$	0.03$^{(C)}$	1.51$^{(B,C,D)}$	2.35$^{(E)}$	0.092$^{(B,C,D)}$	3.71$^{(E)}$	0.32$^{(B,C,D)}$	3.57$^{(E)}$	0.94	0.94	0.94

* Gaseous effluent streams

(A) References 4262 and 2359
(B) Plus approx. 15,000 scfm of reactor off-gases
(C) Plus other diluent gases
(D) Plus 20,000 scfm of dilution air
(E) Plus 1.47 x 10^6 gal scrubbing water
(F) Assumes no lime addition to gypsum ponds.

NOTE: Composition of streams 3, 4 and 5 are given in the uncontrolled mass balance.

Source	Soluble Fluoride Emissions = lb F/ton P_2O_5 Produced Process A	Process B	Process C
Control Device Emission	0.38	0.088	0.20
Wet Process Phosphate Acid Gypsum Ponds	3.14	3.14	3.14
Total Soluble Fluoride Emission	3.52	3.23	3.34

Overall soluble fluoride emission factor from wet process phosphoric acid plants (F) (including gypsum ponds) = 3.36 lb F/ton P_2O_5 produced.

B

Figure 3-31. Wet-Process Phosphoric Acid Production — Controlled Process Models

The state of the art with regard to pollutant collection and removal from wet phosphoric acid manufacture must be rated as good since almost any desired collection efficiency can be achieved by the design and application of appropriate control devices. Liquid collection systems using either fresh or recirculated water have proven efficient in the collection of silicon tetrafluoride and hydrogen fluoride. Adequate particulate collection can also be achieved with the ejector venturi and cross-flow packed scrubber being the most efficient collectors in this regard. The major single consideration in sustaining the high collection efficiencies which new equipment is capable of providing is proper maintenance of control process equipment. Without such maintenance on a continuous basis, collection efficiencies and removal efficiencies drop at an exponential rate, due to plugging, corrosion, and erosion.

The principle soluble fluoride emission sources in phosphoric acid manufacture are the acid and rock mixing points, reactor (digester) tanks, and the liquid filtering units. Reactor tanks are generally closed systems with the free space maintained at pressures slightly below ambient atmosphere. The other emission sources are also hooded. Gaseous effluents from the emission sources are transported through large ducts at moderate linear velocities to the abatement devices and prime movers. The transfer system ducts are frequently rectangular in cross section with removable lids or plates to permit frequent wash out for removal of silica hydrate gel. Duct system linear velocities in plants equipped with vacuum flash coolers range from 5 to 50 feet per second. Slurry transport launders, which recycle material to the digester tanks, normally vent to the free space of the digester tanks. Tilting pan filter hood systems normally collect fune evolution from only the "32% acid" and "first wash" sections of the filter, using sheet rubber flaps to form make-and-break flexible seals with the filter pans as they rotated. "Thirty-two percent acid" and "first wash" filtrate receivers are normally the only filtrate receivers vented to fluoride emission control devices, and in many facilities they are vented directly to the atmosphere. The digestion chambers and filtering units are the primary sources of atmospheric contaminants. Additional sources associated with phosphoric acid manufacture are the evaporators, which are used to concentrate the product acid, and the waste water ponds used for the storage of gypsum and scrubbing water. Evolutions from the acid concentration (evaporation) units are absorbed in the cooling water used in the vacuum system barometric condensors. The primary fluoride emissions are silicon tetrafluoride and hydrogen fluoride. In addition to the major sources of fluoride emissions, there are many miscellaneous minor sources. Process vents from such sources as the phosphoric acid tanks and transfer facilities release exhaust gases to the atmosphere.

One of the primary unsolved problems relating to fluoride emission in the wet phosphoric acid manufacturing industry, and in the entire phosphate rock processing industry, is the ultimate disposal of the fluoride collected by the wet scrubbing systems used to reduce atmospheric pollution. Volatilization of fluorides from gypsum/scrubber recirculation ponds represents a significant portion of the overall emissions. The solution—liming of the gypsum ponds—is employed by only a few of the processors.

Fluoride Emissions. The fluorides evolved from wet process acid manufacture consist primarily of gaseous SiF_4 and HF emanating from the digestors, filters, and various sumps and vents. Since the entire process involves liquid streams, particulate evolution is quite low with only minor quantities of rock emitted from grinding, handling, and process streams. In terms of fluoride evolution, an anomalous situation exists for the acid concentration step. Approximately 70% of the fluoride in weak acid is volatilized in the concentration process. However, the water vapor is recondensed in the barometric condensers in the vacuum system which results in collection of almost all of the fluoride. Since this collection is accomplished as an intrinsic part of the process and no specific collection device is required, this volatilization and recapture of fluoride will be considered internal to the process and not a fluoride evolution. This distinction could not be made for acid concentration by submerged combustion; however, submerged combustion is no longer used significantly, partially because of extensive fluoride evolution. A parallel situation exists for cooling of the digestor slurry where vacuum cooling has displaced air cooling. In both cases, the quantity of soluble fluorides volatilized from the gypsum pond due to barometric scrubber discharges is allocated to phosphoric acid.

Fluoride evolution and emission data have been published for various facilities and circumstances. The values reported typically do not include adequate information to allow calculation of emission factors and a material balance. Public Health Service document AP-57, "Atmospheric Emissions from Wet Process Phosphoric Acid Manufacture,"(4262) presents the most comprehensive data available since it includes plant type, capacity, production rate, equipment descriptions, fluoride evolution and emission factors, concentrations, etc. The evolution and emission factors and effluent concentrations reported in AP-57 are consistent with RRI experience for similar processes and with data from other sources such as Huffstutler and Starnes; therefore, AP-57 will be considered the prime data source for evaluation of evolution and emissions from wet phosphoric acid manufacture. A summary of the reported evolution factors is presented in Table 3-47. Concentration levels for soluble fluorides as fluorine were 3 to 40 ppm or 0.0011 - 0.0147 gr/scfm.(4262) It is apparent from examination of this table that the range of possible evolution factors and concentrations is very large. It should also be considered that these data were likely to have been obtained under the best conditions for minimum evolution. The actual evolution factors in a given case are dependent on such parameters as feed material analysis, acidulation ratio, operating temperature, and quality of processing equipment and maintenance. High range evolution factors appear to be on the order of 2 to 3 pounds of fluoride per ton of P_2O_5 produced. Evolution factors of this magnitude are believed to result when well-designed facilities are properly operated and maintained. Much higher evolution rates may be observed in some cases when improper maintenance or operation of the facility creates operating conditions which preclude operation at low fluoride outputs. If monitoring of fluoride concentration indicates evolution factors significantly above the 2 to 3 pounds per ton of P_2O_5 level, the need for corrective action should be recognized. In a similar manner, well-designed scrubber installations should run above 85% efficiency and in some cases in the high 90% efficiency range. If a scrubber of good basic design drops below this range of values, some operational problem probably exists. Typically, such problems result from deposition of hydrated silica within the scrubber packing or water nozzles so that the liquid-vapor contact is affected.

Table 3-47. Summary of Evolution Factors, and Emission Factors from Reference 4262

Process Element	Evolution Factor (pounds soluble fluorides as fluorine/ton P_2O_5)	Emission Factor (pounds soluble fluorides as fluorine/ton P_2O_5)
Digester/Reactor	0.037 - 2.16	
Filter	0.011 - 0.063	
Sump and Vents	Up to 0.26	
TOTAL		0.006 - 0.17*

*9 out of 10 plants

The material balance is important in determination of the disposition of fluoride in the various streams associated with phosphoric acid production. In this connection, the material balance presented on page 14 of AP-57 was evaluated and found to be inconsistent with the experimental data presented in the same document. Since the reported material balance data were therefore questionable, the AP-57 experimental data for the digestor evolution were combined with the TVA data to serve as a basis for the proportioning of fluoride distribution in other streams. The resulting fluoride distribution is shown in Table 3-48. The maximum total fluoride evolved in the three gaseous streams is approximately 2.5 pounds fluoride per ton P_2O_5.

Emission factors from wet process acid plants range from 0.003 to 0.3 pound of soluble fluorides expressed as fluoride per ton P_2O_5 according to RRI experience over a range of equipment types and sizes. The equivalent range from AP-57 is 0.006 to 0.6 pound per ton.

The soluble fluorides emitted by wet process phosphates and plants are estimated at 6380 tons for 1970, and are projected to reach 21,800 tons per year in 2000 if current practices are continued. If technology capable of 99% effectiveness is adopted and properly maintained, emissions in 2000 will drop to 260 tons per year.

Table 3-48. Fluoride Distribution for Wet Process Phosphoric Acid

Process Stream	Factor (pound fluorine/ton P_2O_5)
Reactor/Digester Gaseous Effluent	0.04 to 2.2
Filter Gaseous Effluent	0.01 to 0.063
Sump and Vent Gaseous Effluent	Up to 0.26
Gypsum	97.5
Evaporation	79.2
Acid	32.6

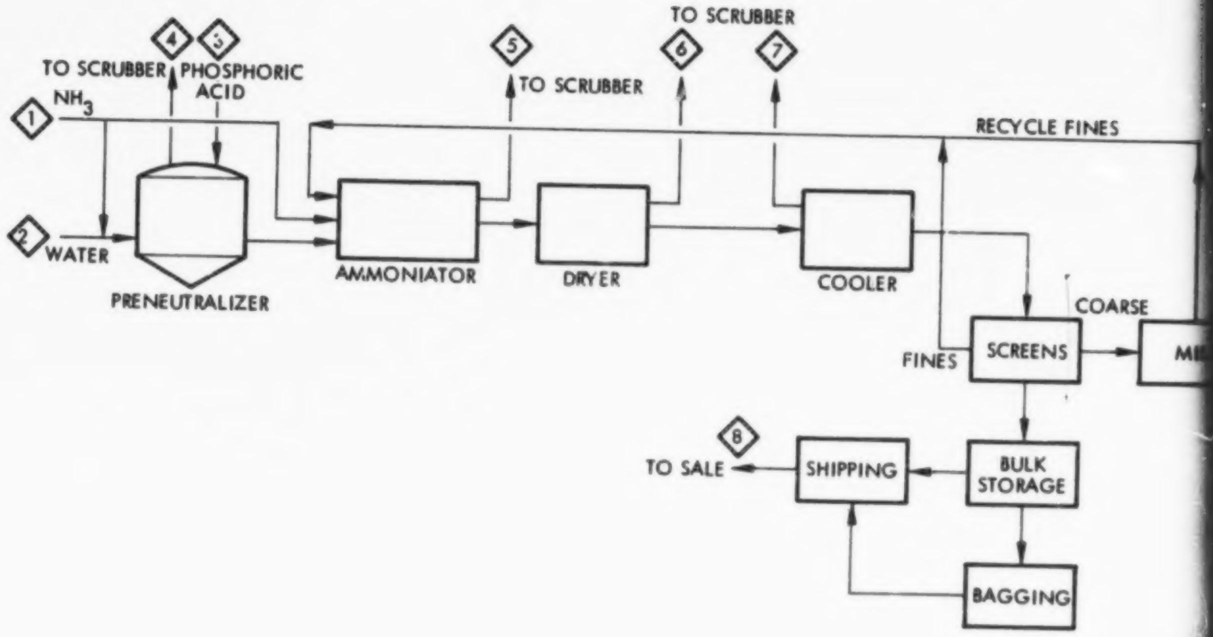
3.5.5.2 Ammonium Phosphates

Process Description. The term "ammonium phosphates" describes a large number of products prepared by combining phosphoric acid, sulfuric acid, ammonia, TSP, urea, and potash to make various nitrogen-phosphorus-potassium (N-P-K) materials. About three-fourths of ammonium phosphate production is accounted for by diammonium phosphate (DAP) which is typically 18-46-0 material (18% nitrogen, 46% available P_2O_5, and 0% K_2O.

DAP will be considered representative for the purpose of evaluating evolution and emission of fluorides from all ammonium phosphates since it is by far the largest individual product and process data for DAP are readily available. Figure 3-32 presents a process schematic for DAP.

Production Trends. Ammonium phosphate production will increase from 2.4 million tons (as P_2O_5) in 1970 to 7 million tons in 2000.(4264)

Fluoride Emission Control Techniques. The wet process phosphoric acid used in the manufacture of diammonium phosphate is the source of fluoride emissions from the process. Wet process acid of the concentration employed



1
NH3
2
WATER
4
TO SCRUBBER
3
PHOSPHORIC ACID
PRENEUTRALIZER
5
TO SCRUBBER
AMMONIATOR
TO SCRUBBER
6
7
DRYER
COOLER
RECYCLE FINES
COARSE
FINES
SCREENS
MI
8
TO SALE
SHIPPING
BULK STORAGE
BAGGING

A

INES
COARSE
MILL

BASIS: 500 TONS/DAY 18-46-0 DIAMMONIUM PHOSPHATE

PROCESS STREAMS TONS/DAYS

Material	1	2	3	4*	5*	6*	7*	8
NH_4F Equiv.					0.067(g)$^{(C)}$	0.067(g)$^{(C)}$	0.02(g)(Est)	
H_2SiF_6 Equiv.			7.8(1)$^{(A)}$	0.08(g)(Est)				
CaF_2 Equiv.								12.5(s)
Total Fluoride			7.8	0.08	0.067	0.067	0.02	12.5
Total As F			6.2	0.06	0.034	0.034	0.02	6.1
NH_3	105(g)$^{(B)}$			2(g)$^{(C)}$	1(g)(Est)	1(g)(Est)		
Phosphoric Acid(45% P_2O_5)			495(1)$^{(B)}$					
H_2O		66(1)		50(g)$^{(C)}$	81(g)(Est)	42(g)(Est)	5(g)(Est)	
18-46-0 Diammonium Phosphate (1% wt Moist)								488(s)
TOTAL IN STREAM	105	66	511	52	82	43	5	500

* Gaseous effluent stream

(A) Reference 4244

(B) References 506 and 4244

(C) Reference 4299

Soluble fluoride evolution factor = 1.3 lb F/ton P_2O_5 in product.

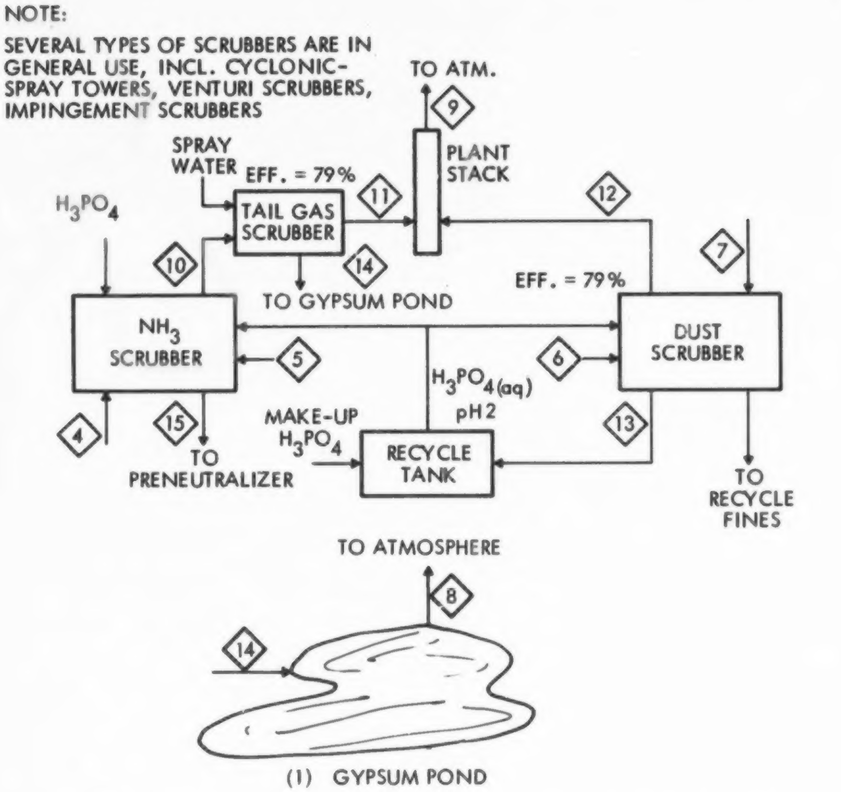
Figure 3-32. Diammonium Phosphate Production-Uncontrolled Process Model

B

generally contains around 2% fluoride. Less fluoride is evolved in the manufacture of either normal or triple superphosphate fertilizer. The primary emission sources for fluoride are the reactor/granulator system and the dryer. Two different scrubber systems are generally used by diammonium phosphate plants. The first system is used to recover ammonia escaping from the reactor and to control gaseous fluorides evolved in the reactor and ammoniator/granulator. The ammonia scrubber and preneutralizer used in the TVA diammonium phosphate process are closed vessels which are vented via large ducts. Evolved gases are transferred from the preneutralizer under induced draft to the ammonia scrubber and fluoride control equipment. The granulator is similarly vented. The second control system is used to control dryer evolution and the dust generated by the screening operations. Liquid scrubbing systems are typically used for the control of both exhaust gas streams. The scrubbing liquid in the first system is the wet process phosphoric acid used in the process. This liquid, which is recycled, has a high fluoride content (about 8000 ppm) and is acid (pH from 2 to 4.5).

Control devices for diammonium phosphate production facilities are generally chosen at the time of plant construction. Devices in general consist of cyclonic spray towers, venturi scrubbers, and impingement scrubbers. Each of these device types have proven efficient in reducing fluoride emissions to acceptable levels. Generally, design is such that maintenance procedures are simple and effective enough to allow the control device to be maintained at the original design operating efficiency. Optimum conditions for the recovery of ammonia, that is, pH of 4.5 or lower and absorption system temperatures of about 160°F, may also cause fluoride to be stripped from the ammonia scrubber liquid and re-enter the exhaust gas stream.

The wet scrubbing devices used in the second scrubbing system must provide a satisfactory collection efficiency for gaseous fluorides at low fluoride concentrations in the exhaust gas stream and efficiently remove particulate material containing 1 to 2% fluoride. In this case, the exhaust gas effluent is generated by the cooling, drying, and sizing sections of the diammonium phosphate processing plant. A controlled process model is presented as Figure 3-33.


NOTE:
SEVERAL TYPES OF SCRUBBERS ARE IN GENERAL USE, INCL. CYCLONIC-SPRAY TOWERS, VENTURI SCRUBBERS, IMPINGEMENT SCRUBBERS
TO ATM.
9
SPRAY WATER
EFF. = 79%
11
PLANT STACK
12
H_3PO_4
TAIL GAS SCRUBBER
10
14
TO GYPSUM POND
EFF. = 79%
7
NH$_3$ SCRUBBER
5
6
DUST SCRUBBER
$H_3PO_{4(aq)}$
pH 2
MAKE-UP H_3PO_4
4
15
TO PRENEUTRALIZER
RECYCLE TANK
13
TO RECYCLE FINES
TO ATMOSPHERE
8
14
(1) GYPSUM POND

(1) A FEW PLANTS LIME THEIR GYPSUM PONDS TO pH 4 TO DECREASE FLUORIDE EVOLUTION

Materials	4	5	6
NH_4F equiv.	0.08(g)	0.067(g)	0.067(g)
Total Fluorides Total as F	0.08 0.041	0.067 0.0345	0.067 0.0345
NH_3 H_2O	2(g) 50(1)	1(g) 81(g)	1(g) 42(g)
Approx. Total Stream	52	82	43

* Gaseous Effluent Stream

Source	Soluble Fluoride E
Stack Emission	
DAP Gypsum Pond Emission	
Total Soluble Fluoride Emission	

Overall soluble fluoride emission factor for d

0.23 lb F/ton P_2O_5 in product

A

BASIS - 500 TONS/DAY

PROCESS STREAMS - TONS/DAY

Stream Number											
4	5	6	7	8*	9*	10	11	12	13	14	15
(g)	0.067(g)	0.067(g)	0.02(g)	0.002(g)(Est)	0.049(g)$^{(D)}$	0.147(g)	0.031(g)	0.018(g)	0.069(g)	0.116(1)	
	0.067 0.0345	0.067 0.0345	0.02 0.010	0.002 0.001	0.049 0.025$^{(D)}$	0.147 0.075$^{(D)}$	0.031 0.016$^{(D)}$	0.018 0.009$^{(D)}$	0.069 0.035$^{(D)}$	0.116 0.060$^{(D)}$	
	1(g) 81(g)	1(g) 42(g)	5(g)						1(1) 47(1)		3(1) 131(1)
	82	43	5	--	0.049	0.147	0.031	0.018	48$^{(A)}$	0.116$^{(B)}$	134$^{(C)}$

am

(A) Plus recycling H_3PO_4 containing 8000 ppm F

(B) Plus scrubbing water

(C) Plus ammoniated H_3PO_4

(D) Reference 4267

(E) Assumes no line addition to gypsum ponds

Soluble Fluoride Emission Factor - lb F/ton P_2O_5 in product
0.22
0.009
0.23

emission factor for diammonium phosphate production (including gypsum ponds) =

oduct

Figure 3-33. Diammonium Phosphate Production — Controlled Process Model

B

Fluoride Emissions. Fluoride input to the process is from the wet process phosphoric acid. The acid is typically used at a concentration of about 40 percent P_2O_5. Such acid has a fluoride content of about 93 pounds fluoride/ton P_2O_5. This residual fluoride content has been retained through the acid production process and is relatively stable under the conditions associated with DAP production. Evolution occurs at the reactor/granulator and the dryer and screens. Table 3-49 presents the fluoride evolution and emission from manufacture of DAP.(4299) Based on Table 3-49 values, the annual fluoride evolution from ammonium phosphate production is 966 tons fluoride per year. The annual soluble fluoride emission is 161 tons fluoride per year. These values were generated utilizing a 3,222,000 tons P_2O_5 per year production rate for ammonium phosphate as reported in preliminary form under the Engineering and Cost Study of Emissions Control in the Phosphate Industry (CPA 70-156).

Table 3-49. Evolution and Emission of Fluorides from Production of Ammonium Phosphates

Process Evolution Source	Evolution (pounds soluble fluorides as fluorine/ton P_2O_5)	Emission (pounds soluble fluorides as fluorine/ton P_2O_5)
Preneutralizer/ Ammoniator	0.3	0.05
Dryer/Cooler/Screens	0.3	0.05
TOTAL	0.6	0.1

3.5.5.3 Triple Superphosphate

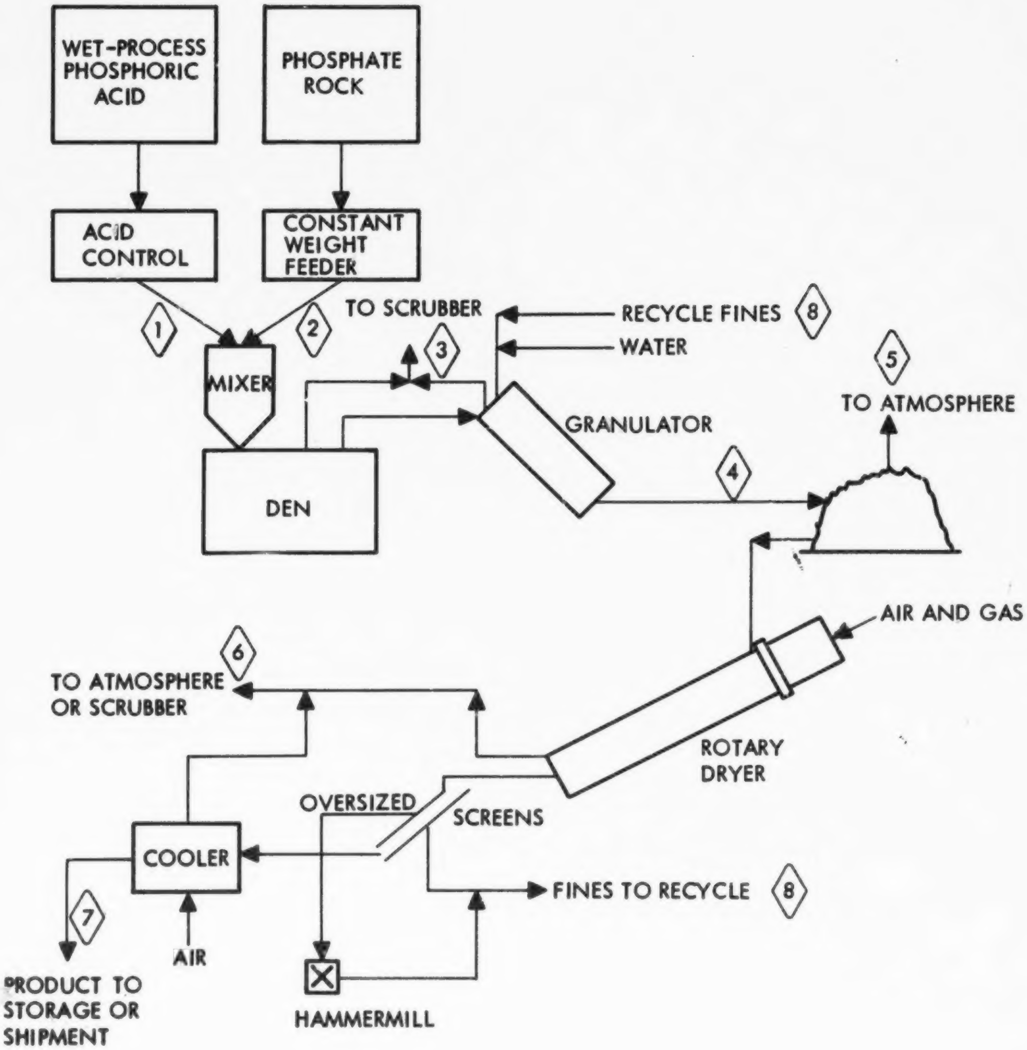
Process Description. Triple superphosphate (TSP) is made by acidulating phosphate rock with wet process phosphoric acid. The product may be in either pulverized or granular form; the P_2O_5 content is approximately 46%. TSP is relatively concentrated, which minimizes shipping costs, and the phosphorus content is almost entirely in plant available form. Detailed information on chemistry, processes, and equipment is available in References 4242, 4263, 4264, and 4265.

Figure 3-34 is a typical process diagram for production of granulated triple superphosphate. Production of granular triple superphosphate will be considered as typical of the problems since "run-of-pile" production is decreasing rapidly.

Production Levels. Triple superphosphate will increase from a 1970 level of 1.4 million tons to 2.7 million tons in 2000(4264).

Fluoride Emission Control Techniques. Run-of-pile (ROP) triple superphosphate setting belts and disintegrators are hooded and maintained at slightly below ambient pressure. Gaseous effluents are transported at moderate linear velocities through large ducts which are generally rectangular in cross-section. Conveyor belts transporting the fresh ROP triple superphosphate to the storage building are, to an indeterminate extent, hooded and vented to the storage building. Most triple superphosphate storage buildings are maintained slightly below ambient pressure and are vented through roof outlets to fluoride control devices and prime movers. Screens and mills for processing cured triple superphosphate are hooded and vented through circular ducts to the cyclones and then to prime movers.

The acidulators employed in granular triple superphosphate manufacture are closed vessels maintained slightly below ambient pressure and vented to fluoride control equipment. The launders between tanks vent to the free space of the acidulators. The granulator and dryer are hooded as are the screens and crusher. Transfer ducts for dust and gaseous pollutant laden effluent gas streams are provided with clean-out plates in the form of removable ports or lids. The controlled process model is presented in Figure 3-35.


WET-PROCESS PHOSPHORIC ACID
PHOSPHATE ROCK
ACID CONTROL
CONSTANT WEIGHT FEEDER
1
2
TO SCRUBBER
3
RECYCLE FINES
8
WATER
MIXER
DEN
GRANULATOR
5
TO ATMOSPHERE
4
AIR AND GAS
6
TO ATMOSPHERE OR SCRUBBER
ROTARY DRYER
OVERSIZED
SCREENS
COOLER
FINES TO RECYCLE
8
7
AIR
PRODUCT TO STORAGE OR SHIPMENT
HAMMERMILL

BASIS - 200 T

Material	1
H_2SiF_6 (equiv.)	
SiF_4	
CaF_2 (equiv.)	7.4(s)$^{(B)}$
Total Fluoride	7.4(s)
Total as F	3.6(s)
Triple Superphosphate 48% P_2O_5	
Wet Process Phosphoric Acid 54%	
Phosphate Rock 32.3% P_2O_5	83(s)$^{(B)}$
H_2O	
Approx. Total Stream	90

F Evolution Factor = 21 lb F/to

* Gaseous effluent stream

(A) Plus combustion products a
(B) Reference 4264
(C) Reference 506

Soluble fluoride evolution fact

A

BASIS - 200 TONS PRODUCT/DAY (48% P_2O_5)

PROCESS STREAMS (TONS/DAY)

rial	Stream Number							
	1	2	3*	4	5*	6*	7	8
(equiv.)		3.0(l)$^{(B)}$	0.64(g)$^{(C)}$		0.73(g)$^{(C)}$	0.07(g)$^{(C)}$		
quiv.)	7.4(s)$^{(B)}$			12.9(s)			10.16(s)	1.5(s)
luoride	7.4(s)		0.64	12.9	0.73	0.07	10.16	1.5
s F	3.6(s)	2.4	0.47	6.28	0.53	0.05	4.95	0.75
Super- te 5				217(s)			190.0(s)	28.0(s)
cess ric Acid		129(l)$^{(B)}$						
te Rock $_2O_5$	83(s)$^{(B)}$							
			15(g)		5.0(g)	2.0(g)		
Total	90	132	16	230	60	2	200	30

tion Factor = 21 lb F/ton P_2O_5

s effluent stream

s combustion products and diluent air

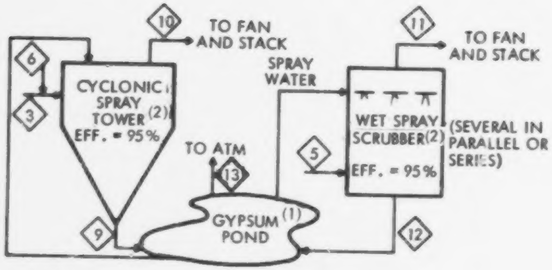
ference 4264

ference 506

fluoride evolution factor = 21 lb F/ton P_2O_5 produced.

B

Figure 3-34. Granulated Triple Super Phosphate Production — Uncontrolled Process Model



6
3
CYCLONIC SPRAY TOWER (2)
EFF. = 95%
10
TO FAN AND STACK
TO ATM
13
GYPSUM (1) POND
9
SPRAY WATER
5
WET SPRAY SCRUBBER (2)
EFF. = 95%
(SEVERAL IN PARALLEL OR SERIES)
11
TO FAN AND STACK
12

NOTE:

(1) SOME PLANTS LIME THEIR GYPSUM PONDS TO pH 4 TO REDUCE HF EVOLUTION

(2) REFLECTS OPTIMUM OPERATING AND MAINTENANCE CONDITIONS

BASIS - 200 TONS/DAY (48% P_2O_5)

PROCESS STREAMS-TONS/DAY

Materials	Stream Number							
	3	5	6	9	10*	11*	12	13*
H_2SiF_6				0.62(1)			0.63(1)$^{(D)}$	
SiF_4	0.64(g)	0.73(g)	0.07(g)					
HF					0.03(g)$^{(D)}$	0.03(g)$^{(D)}$		0.01(g)(Est)
Total Fluorides	0.64	0.73	0.07	0.62	0.03	0.03	0.63	0.01
Total as F	0.47	0.53	0.05	0.49	0.03	0.03	0.50	0.01
H_2O	15(g)	5.0(g)	2.0(g)	17(1)			5.0(1)	
Approx. Total Stream	15.6	5.73$^{(C)}$	2.07	17.6$^{(A)}$	0.03	0.03$^{(C)}$	5.63$^{(B)}$	0.01

* Gaseous Effluent Streams

(A) Plus 67,000 gal recycled scrubbing water

(B) Plus recycled scrubbing water

(C) Plus 33 x 10^6 scf air

(D) Reference 4267

(E) Estimate average industry abatement efficiency of 75% caused by improper maintainance and operation of equipment and fugitive sources.

Source	Soluble Fluoride Emission Factor - lb F/ton P_2O_5 Produced (assuming optimum conditions)	Soluble Fluoride Emission Factor - lb F/ton P_2O_5 Produced (assuming average industry operation)
Control Device Emissions	1.2	5.2
TSP Gypsum Ponds	0.2	0.2
Total Soluble Fluoride Emission	1.4	5.4

Overall soluble fluoride emission factor from triple superphosphate plants (including gypsum ponds) = 5.4 lb F/ton P_2O_5 produced. (E)

Figure 3-35. Manufacture of Granular Triple Superphosphate — Controlled Process Model

Fluoride Emissions. Fluorides enter the TSP process in the phosphate rock and in the wet process acid. They are volatilized and evolved during acidulation, digestion, and curing. In contrast to the wet acid and elemental phosphorus processes, manufacture of TSP does not include a direct contact condensation step as part of the basic process and does involve transport of solids on conveyor belts as opposed to transport of liquids in closed systems. The former characteristic means that any fluoride captured to reduce emissions is caused by installation of control equipment. The latter characteristic means that the processing system is not sealed as a matter of course; conveyor belts, transfer points, etc., are all potential emission sources if they are not hooded in some appropriate manner. After acidulation and completion of the initial reaction, TSP is stored and cured in large buildings for several weeks to complete the reactions converting the phosphorus present to an available form. During this time period, fluorides continue to evolve at a much lower rate than for the initial reaction steps. This long-term, low-level evolution, if uncontrolled, may constitute the major portion of the emissions from a TSP manufacturing facility.

The process presented in Figure 3-34 is one of several currently used for the production of granular TSP. An alternative, widely used process is the Dorr-Oliver process. Data for the run-of-pile, and Dorr-Oliver granulated TSP processes are presented in Table 3-50, covering the evolution and emission factors for various source points in the TSP processes. The rate of evolution of fluorides from the manufacture of TSP is dependent on many factors, e.g., rock composition, acid/rock ratio, and temperature. The reported values are based on RRI experience with several processes. The emissions factors of Table 3-50 are based on the assumption that the emissions from mixers, dens, reactors, and granulators, are controlled while conveyors and cure buildings may or may not be. It is apparent that the fluoride emitted can be reduced to low levels by application of appropriate fume capture and control equipment (hooding and wet scrubbers). However, any uncontrolled emission, even from a low level source such as the cure building, becomes the dominant emission value and determines the process emission

Table 3-50. Evolution and Emission Factors for Triple Superphosphate Manufacture

Product	Emission Source Points*	Evolution Factor (pound soluble fluorides as fluorine/ton P_2O_5)	Emission Factor (pound soluble fluorides as fluorine/ton P_2O_5)
Run-of-Pile	Mixer Den Conveyor	3	0.1
	Cure Building	3	0.3 - 3
	TOTAL	6	0.4 - 3.1
Granulated	Reactor-Granulator	9	0.01
	Dryer	12	0.3
	Cure Building	3	0.3 - 3
	TOTAL	24	0.6 - 3.3

*Evolved material from various points combined and routed to control device.

factor. The higher evolution factor for granulated TSP is partially due to utilization of less concentrated acid which contains more fluoride and to higher temperature processing with application of heat for drying.

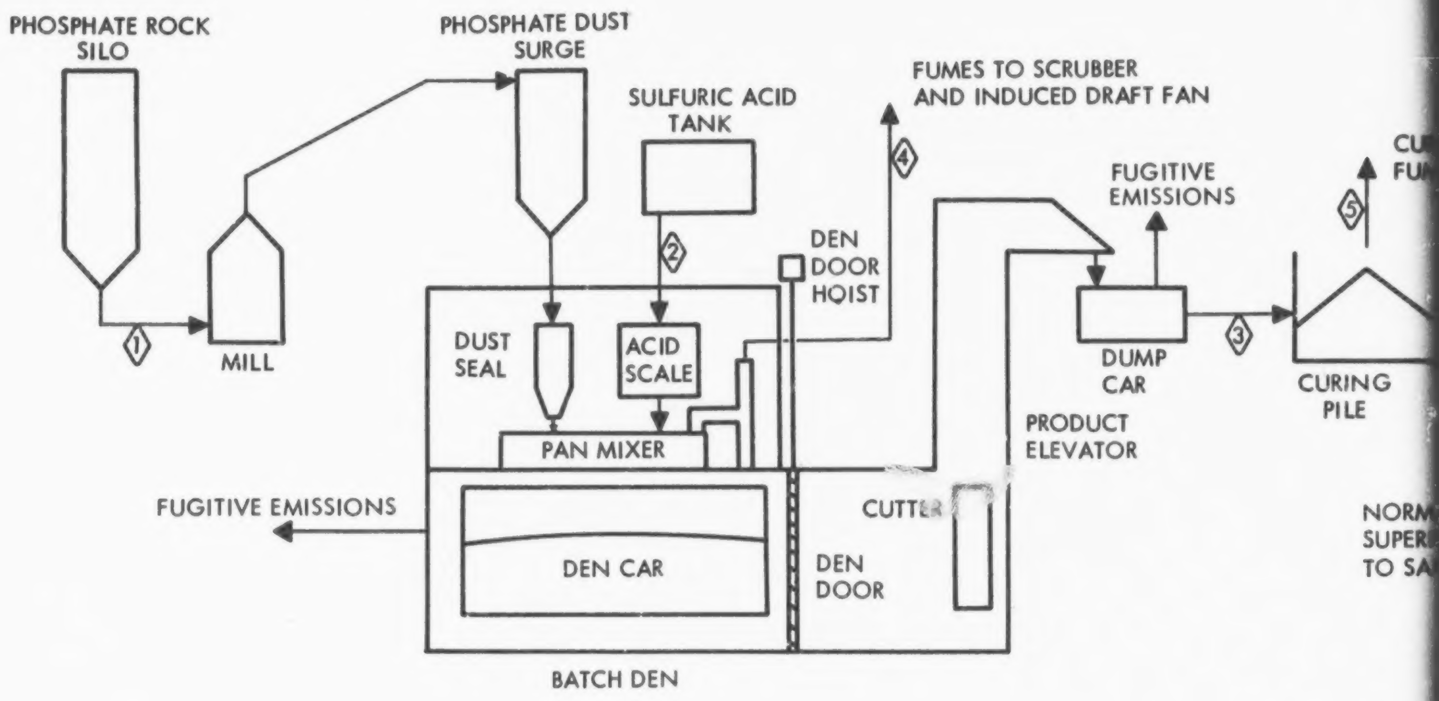
It is estimated that 3780 tons of soluble fluorides (expressed as F) were emitted in 1970, and that, on the same basis, assuming current control efficiencies, 7290 tons will be emitted in 2000. If 99% efficient control techniques are employed, only 280 tons will be emitted in 2000.

3.5.5.4 Normal Superphosphate

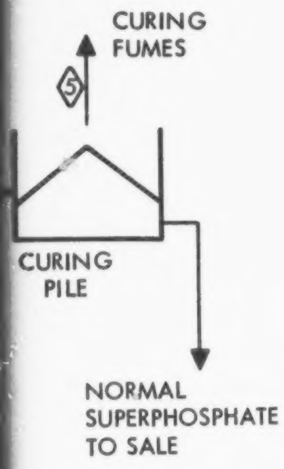
Process Description. Normal superphosphate (NSP) is produced by acidulating phosphate rock with sulfuric acid. The product contains calcium acid phosphates and calcium sulfate with an available P_2O_5 content of about 20 percent. The production rate of NSP has been decreasing yearly as difficulty in competing with more concentrated fertilizers increases. NSP was the first phosphatic fertilizer in major use and many of the production facilities are outmoded. The cost of shipping a 20% available P_2O_5 product and the cost of updating facilities for efficient operation with acceptable air pollution control is accelerating a trend toward reduced NSP production.

NSP can be produced either batchwise or continuously as illustrated in the process schematics in Figures 3-36 and 3-37. In both cases, there are three processing steps involved. These are: mixing of the acid and rock, temporary holding while reacting to form a solid (denning), and storage for completion of reactions (curing). The time scale of the latter two processes are about 1 to 2 hours for denning and about 4 to 6 weeks for curing.

Production Trends. Production of normal superphosphate will drop from 0.7 million tons in 1970 to 0.2 million tons in 2000(4264).


PHOSPHATE ROCK SILO
1
MILL
PHOSPHATE DUST SURGE
SULFURIC ACID TANK
2
DUST SEAL
ACID SCALE
PAN MIXER
DEN DOOR HOIST
FUMES TO SCRUBBER AND INDUCED DRAFT FAN
4
FUGITIVE EMISSIONS
DUMP CAR
3
CURING PILE
5
CU
FU
PRODUCT ELEVATOR
FUGITIVE EMISSIONS
DEN CAR
CUTTER
DEN DOOR
BATCH DEN
NORM
SUPER
TO SA

A



BASIS: BATCH PRODUCTION OF NORMAL SUPERPHOSPHATE (0-20-0) AT 40 TONS PER BATCH (1 BATCH PER HOUR)

PROCESS STREAMS

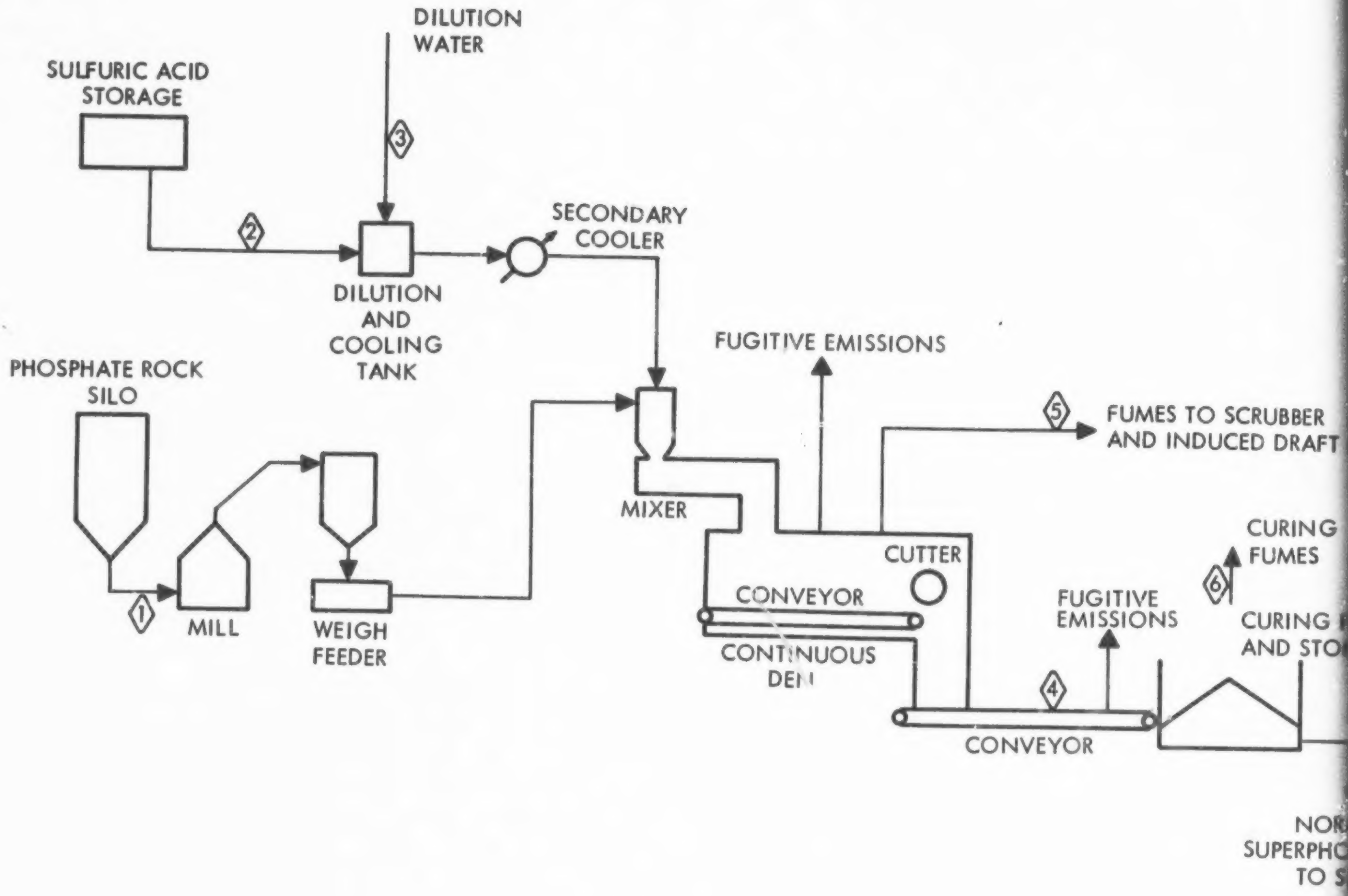
Material Tons/Batch	Stream Process				
	1	2	3	4*	5*
SiF_4 (Equiv.)				$0.36(g)^{(C)}$	$0.04(g)^{(C)}$
CaF_2 (Equiv.)	$1.87(s)^{(C)}$		$1.27(s)^{(C)}$		
Total Fluorides	1.87		1.27	0.36	0.04
Total as F	0.91		0.62	0.26	0.03
Phosphate Rock (75 b.p.l)	$25(s)^{(A)}$				
Sulfuric Acid (54°Be)		$22(l)^{(A)}$			
Normal Superphosphate (0-20-0)			$40(s)^{(C)}$		
Denning Fumes				$13000(g)^{(B)}$**	
Curing Fumes					$0.03\ (g)^{(C)}$ ***
Approx. Total Stream	25	22	40	13,000**	0.03***

F Evolution factor = 73 lb F/ton P_2O_5
* Gaseous effluent stream
** SCFM
*** Fluorine component only
Soluble fluoride evolution factor = 73 lb F/ton P_2O_5 produced

(A) Reference 4263
(B) Reference 4267
(C) Reference 4264

Figure 3-36. Normal Superphosphate Batch Production - Uncontrolled Process Model

B


DILUTION WATER
SULFURIC ACID STORAGE
3
2
SECONDARY COOLER
DILUTION AND COOLING TANK
FUGITIVE EMISSIONS
PHOSPHATE ROCK SILO
5
FUMES TO SCRUBBER AND INDUCED DRAFT
MIXER
CURING
FUMES
CUTTER
6
CONVEYOR
FUGITIVE EMISSIONS
1
MILL
WEIGH FEEDER
CONTINUOUS DEN
4
CURING
AND STO
CONVEYOR
NOR
SUPERPHO
TO S

A

BASIS: CONTINUOUS PRODUCTION OF NORMAL SUPERPHOSPHATE (0-20-0)
AT 200 TONS PER DAY

PROCESS STREAMS

Materials Tons/Day	Stream Number					
	1	2	3	4	5*	6*
SiF_4 (equiv.)					$1.68(g)^{(A)}$	$0.19(g)^{(A)}$
CaF_2 (equiv.)	$8.91(s)^{(A)}$			$6.10(s)^{(A)}$		
Total Fluorides	8.91			6.10	1.68	0.19
Total as F	4.34			2.97	1.23	0.14
Phosphate Rock (75 b.p.l.)	$120(s)^{(A)}$					
Sulfuric Acid (66°Be')		$75(l)^{(A)}$				
Water			$30(s)^{(A)}$			
Normal Super-Phosphate (0-20-0)				$200(s)^{(A)}$		
Denning Fumes					$2600(g)^{**}$ (B)	
Curing Fumes						$0.14(g)^{(A)}$***
Approx. Total Stream	120	75	30	200	2600**	0.14***

* Gaseous effluent stream

** SCFM

*** Fluorine component only

(A) Reference 4263

(B) Reference 4267

Soluble fluoride evolution factor = 69 lb F/ton P_2O_5 produced

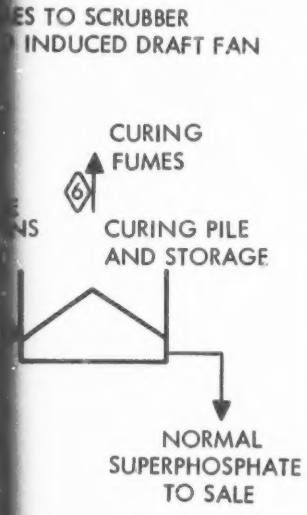

ES TO SCRUBBER
INDUCED DRAFT FAN
CURING FUMES
6
E
NS
CURING PILE AND STORAGE
NORMAL SUPERPHOSPHATE TO SALE

Figure 3-37. Normal Superphosphate Continuous Production — Uncontrolled Process Model

B

Fluoride Emission Control Techniques. In both continuous and batch processes for normal superphosphate manufacture, there are several points of fluoride emission. Particulate fluorides are produced by the grinding and drying operations performed on the phosphate rock prior to its acidulation and by product handling. Gaseous fluorides, primarily silicon tetrafluoride, are produced and emitted during acidulation, denning, transport, and curing processes. The major portion of fluoride evolution occurs during acidulation and denning with only minor evolution during the cutting and bulk storage cure of the product. Effluent control systems have been designed and applied to collect all significant process emissions associated with normal superphosphate manufacture; however, typical practice may include control of only the mixer and den due to economic constraints. In that case, uncontrolled emissions from transfer and curing may become the dominant emission.

The pan mixer and batch den used in batch manufacture of normal superphosphate are vented through extremely large ducts ("tunnels") to the fluoride control equipment and prime movers. The batch den is a closed vessel during the period of time required for the single superphosphate to "set up" except for the vent duct. When the NSP has "set up," a side of the den is dropped. The cutter is hooded and ducts are provided with clean-out doors. Continuous process superphosphate mixers, dens, and cutters are hooded with the den and other equipment maintained below atmospheric pressure. The air swept into the system and evolved particulate matter and fluoride pollutants are vented through extremely large ducts to fluoride control equipment. The ducts are provided with drains and clean-out doors.

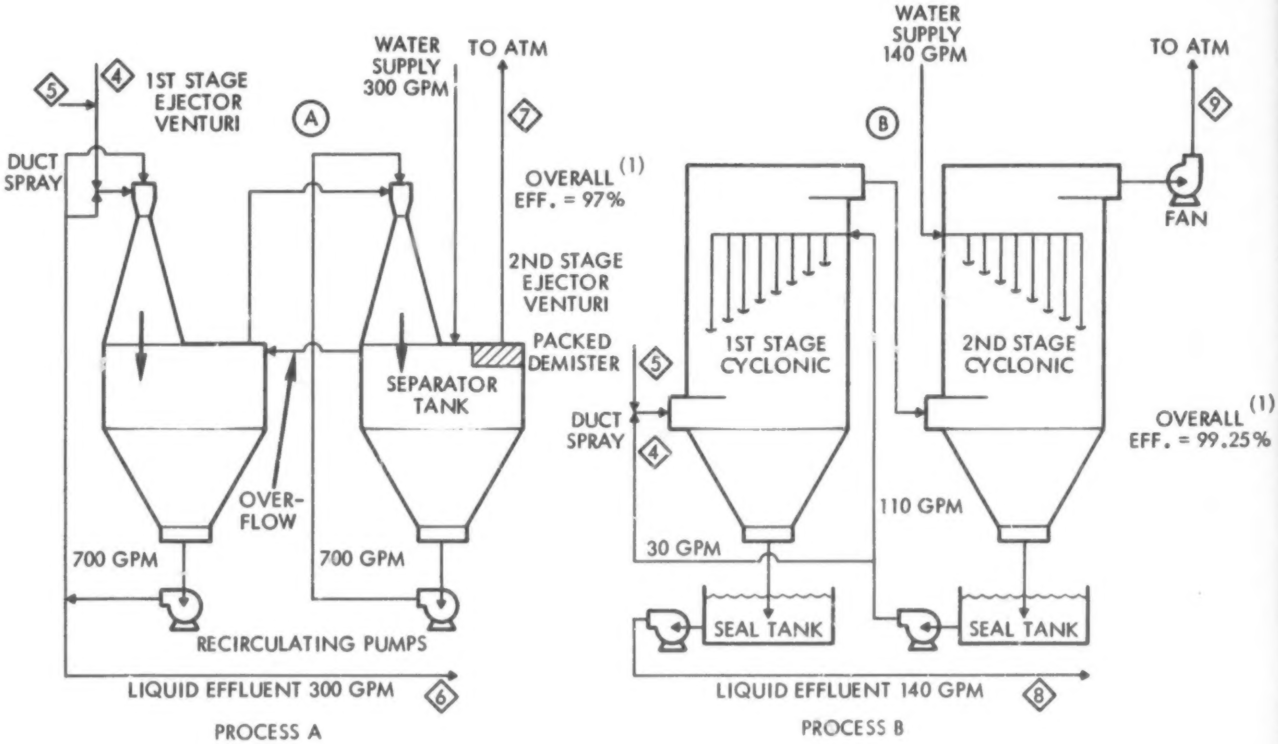
The volume of exhaust gases evolved during the manufacture of normal superphosphate varies greatly from facility to facility. Plant design, tightness of the collection equipment, and the number of pieces of equipment being vented all are factors affecting the exhaust gas volume. The measured exhaust gas flow rates on existing normal superphosphate plants ranges from 3,000 to 35,000 actual cubic feet per minute (ACFM). The range in production capacity associated with these exhaust gas volumes is from 6 to 40 tons per hour superphosphate. Continuous plants typically produce a larger volume of exhaust gas than do batch operations. However, the exhaust gas stream from continuous operations generally has a lower fluoride content.

The control of particulate fluoride emissions produced during the rock grinding and drying operations represent a classical dust control problem. Certain dust control devices such as cyclone collectors or baghouses are generally considered to be part of the grinding process equipment. The use of high-efficiency, multi-cyclone collectors and/or fabric filters may produce efficiencies of from 99 to 99.5%. All of the particulate material collected is directly returned to process and so there is no waste disposal problem associated with the particulate fluoride emissions.

The gaseous fluoride emissions produced by phosphate rock acidulation both in the mixer and the curing den are generally controlled by wet scrubbing units. As stated earlier, the principal fluoride emission from this operation is silicon tetrafluoride with some hydrogen fluoride. Spray tower scrubbers are often used to absorb the fluoride compounds. Efficiencies in the range of 90 to 99% are reported for new or well maintained units depending upon the number of scrubbing stages used.

Recently designed normal superphosphate plants often utilize commerical scrubbing equipment of the wet cyclone or ejector venturi type. The gaseous fluoride removal efficiency of these types of equipment is generally in the 95 to 99% range. Recirculation is the universal practice in ejector venturi installations. The control process mass balances are presented as Figures 3-38 and 3-39.

Fluoride Emissions. Fluorides are evolved during all three processing steps in NSP manufacture. Table 3-51 shows typical evolution and emission factors as indicated by RRI experience. The NSP process is similar to the TSP process in that fluorides are evolved while forming and handling a solid product. Collection and removal of this fluoride in an efficient, economical manner is especially difficult since the process

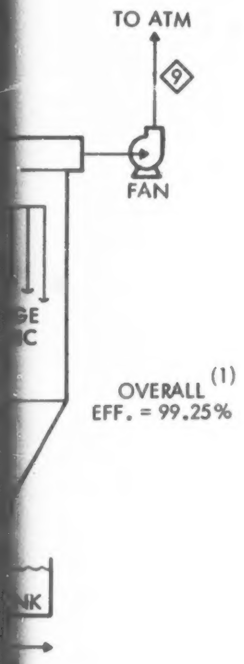

⑤
④
1ST STAGE EJECTOR VENTURI
Ⓐ
WATER SUPPLY 300 GPM
TO ATM
⑦
DUCT SPRAY
OVERALL (1) EFF. = 97%
2ND STAGE EJECTOR VENTURI
PACKED DEMISTER
SEPARATOR TANK
OVER-FLOW
700 GPM
700 GPM
RECIRCULATING PUMPS
LIQUID EFFLUENT 300 GPM
⑥
WATER SUPPLY 140 GPM
TO ATM
⑨
Ⓑ
FAN
1ST STAGE CYCLONIC
2ND STAGE CYCLONIC
⑤
DUCT SPRAY
④
OVERALL (1) EFF. = 99.25%
110 GPM
30 GPM
SEAL TANK
SEAL TANK
LIQUID EFFLUENT 140 GPM
⑧

PROCESS A

PROCESS B

(1) REFLECTS OPTIMUM OPERATING AND MAINTENANCE CONDITIONS

A



BASIS - 40 TONS/BATCH (1 BATCH/HR) (20% P_2O_5)
PROCESS STREAMS-TONS/BATCH

MATERIAL	Stream Number					
	4	5	6	7*	8	9*
SiF_4(Equiv.)	0.36(g)	0.4(g)				
HF				0.009(g)(D)		0.003(g)(D)
H_2SiF_6(Equiv.)			0.355(aq)		0.363(aq)	
Total Fluorides	0.36	0.04	0.355	0.009	0.363	0.003
Total as F	0.26	0.03	0.281	0.009	0.287	0.003
Denning Fumes	13000(g)**			13000(g)**		13000(g)**
Misc. Curing Fumes		0.003(g)		0.003(g)		0.003(g)
Approx. Total Stream	13000**	0.03(A)	0.355(B)	13000** (A)	0.363 (C)	13000**(A)

* Gaseous effluent streams

** SCFM

(A) Plus 14,000 cfm air carrier gas

(B) Plus 300 gpm scrubbing water

(C) Plus 140 gpm scrubbing water

(D) Reference 4267

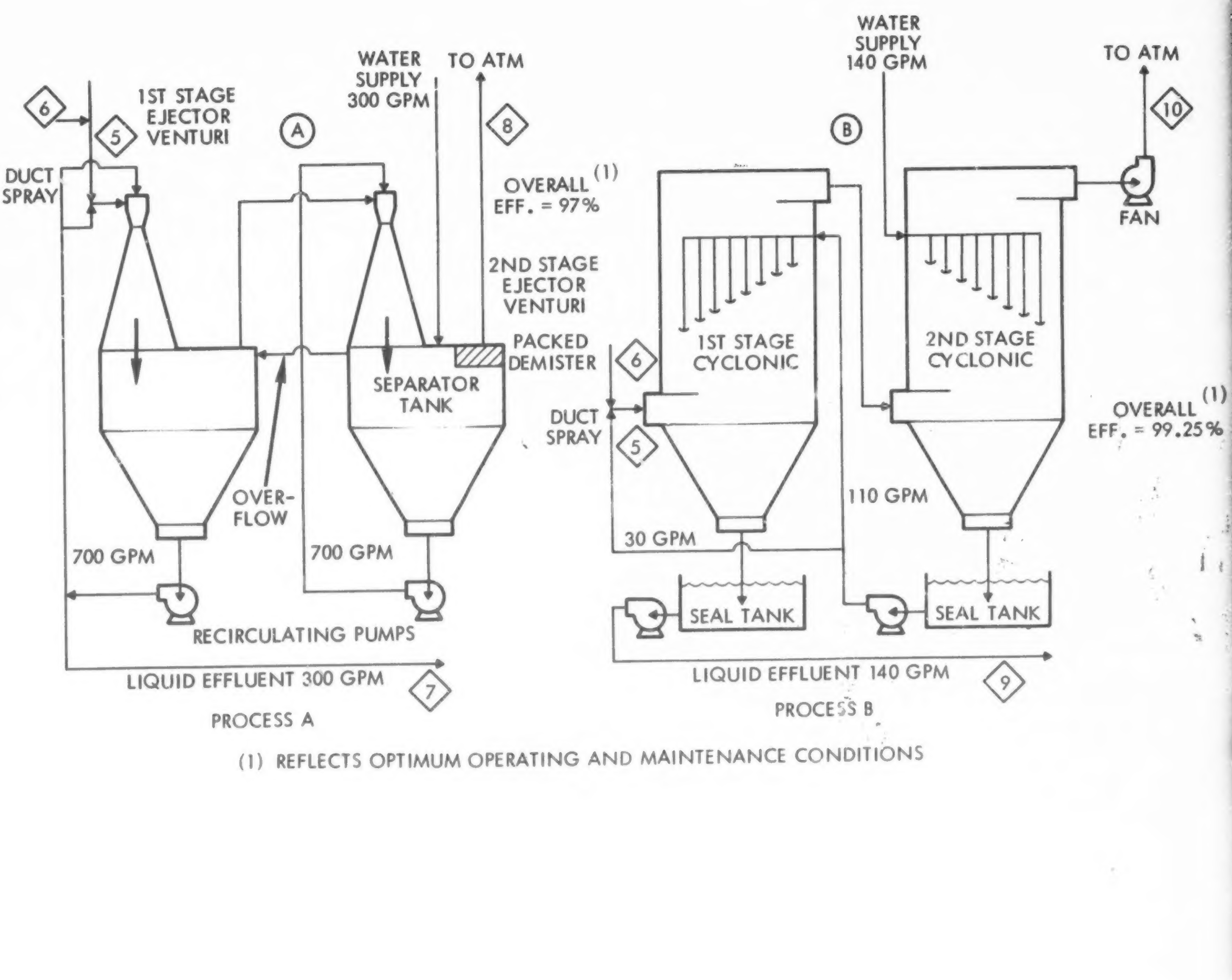
(E) Estimate average device efficiency to be 90% with current maintainance and operation techniques and fugitive emissions equal to 10% of evolution.

Source	Soluble Fluoride Emission Factor - lb F/ton P_2O_5 Produced (Assuming optimum conditions)		Soluble Fluoride Emission Factor - lb F/ton P_2O_5 Produced (Assuming average industry operation)	
	Process A	Process B	Process A	Process B
Control Device Emission	2.3	0.8	7.3	7.3
Assumed Fugitive Emission	0	0	7.3	7.3
Total Soluble Fluoride Emission	2.3	0.8	14.6	14.6

Overall soluble fluoride emission factor = 14.6 lb F/ton P_2O_5 produced (E)

B

Figure 3-38. Normal Superphosphate Batch Production — Controlled Process Model



6
1ST STAGE EJECTOR VENTURI
5
A
WATER SUPPLY 300 GPM
TO ATM
8
DUCT SPRAY
OVERALL (1) EFF. = 97%
2ND STAGE EJECTOR VENTURI
PACKED DEMISTER
SEPARATOR TANK
OVER-FLOW
700 GPM
700 GPM
RECIRCULATING PUMPS
LIQUID EFFLUENT 300 GPM
7
PROCESS A
WATER SUPPLY 140 GPM
TO ATM
10
B
FAN
1ST STAGE CYCLONIC
2ND STAGE CYCLONIC
6
DUCT SPRAY
5
OVERALL (1) EFF. = 99.25%
110 GPM
30 GPM
SEAL TANK
SEAL TANK
LIQUID EFFLUENT 140 GPM
9
PROCESS B

(1) REFLECTS OPTIMUM OPERATING AND MAINTENANCE CONDITIONS

A

O ATM
10
FAN
OVERALL (1)
= 99.25%

BASIS - 200 TONS/DAY (20% P_2O_5)
PROCESS STREAMS-TONS/DAY

MATERIAL	Stream Number					
	5	6	7	8*	9	10*
SiF_4 (Equiv.)	1.68(g)	0.19(g)				
HF				0.04(g)$^{(D)}$		0.01(g)$^{(D)}$
H_2SiF_6 (Equiv.)			1.68(aq)		1.72(aq)	
Total Fluorides	1.68	0.19	1.68	0.04	1.72	0.01
Total As F	1.23	0.14	1.33	0.04	1.36	0.01
Denning Fumes	2600(g)**			2600(g)**		2600(g)**
Misc. Curing Fumes		0.14		0.14		0.14
Approx. Total Stream	2600**	0.33$^{(A)}$	1.68$^{(B)}$	2600(g)**$^{(A)}$	1.72$^{(C)}$	13000**$^{(A)}$

* Gaseous Effluent Streams

** SCFM

(A) Plus 14,000 cfm air carrier gas

(B) Plus 300 gpm scrubbing water

(C) Plus 140 gpm scrubbing water

(D) Reference 4267

(E) Estimate average device efficiency to be 90% with current maintainance and operation techniques and fugitive emissions equal to 10% of evolution.

Source	Soluble Fluoride Emission Factor - lb F/ton P_2O_5 Produced (Assuming optimum conditions)		Soluble Fluoride Emission Factor - lb F/ton P_2O_5 Produced (Assuming average industry operation)	
	Process A	Process B	Process A	Process B
Control Device Emission	2.0	0.5	6.9	6.9
Assumed Fugitive Emissions	0	0	6.9	6.9
Total Soluble Fluoride Emission	2.0	0.5	13.8	13.8

Overall soluble fluoride emission factor = 13.8 lb F/ton P_2O_5 produced $^{(E)}$

Figure 3-39. Normal Superphosphate Continuous Production - Controlled Process Model

Table 3-51. Evolution and Emission Factors for Manufacturing Normal Superphosphate

Source Point	Evolution (pounds soluble fluorides as fluorine/ton P_2O_5)	Emission (pounds soluble fluoride as fluorine/ton P_2O_5
Mixer-Den	68	2
Storage	3	0.3 - 3
Total	71	2.3 - 5

involves many mechanical operations which are difficult to seal effectively. These include den cutting, material transport, and product curing. Even where fume collection and scrubbing is utilized, comparatively low collection efficiency and high air flow requirements can be anticipated if the system leaks or is opened for appreciable periods of time. No information has been found that provides a good basis for estimating leakage losses from denning. The emission factors presented in Table 3-51 do not include such losses. It is clear that improperly sealed or poorly maintained units might involve multiples of the emission factors listed. Soluble fluoride emissions from NSP manufacture are estimated as equivalent to 5000 tons of F in 1970. For the year 2000, if current control practices continue, emissions will be about 1400 tons. If 99% control efficiency is utilized emissions in 2000 would drop to less than 100 tons (expressed as F).

3.5.5.5 Defluorination of Phosphate Rock

Process Description. Phosphate rock can be used as an animal or poultry feed supplement if the fluoride content is reduced to an acceptable level to prevent adverse biological effects. The product must be reduced from about 3.5% fluorine to less than 0.2% fluorine. This reduction is typically accomplished by thermal and/or chemical processing. The heating processes utilize rotary kiln or fluidized bed heaters in which the rock is mixed with additives such as phosphoric acid, silica, etc. to aid in defluorination and heated to 2500° to 2900°F to drive off the fluorides.

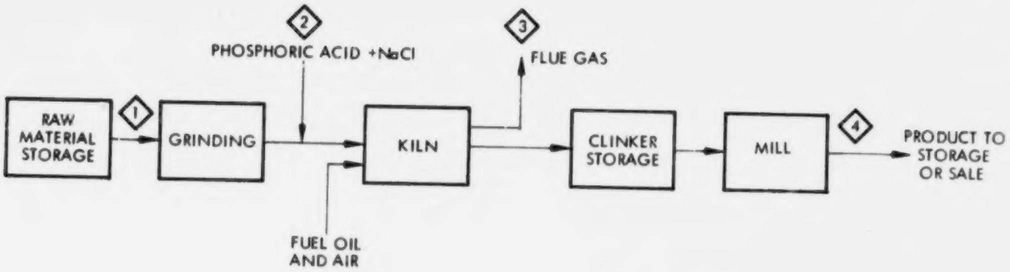
This process is shown in Figure 3-40. An alternate defluorination process involves reacting hot phosphoric acid with limestone thereby precipitating and volatilizing fluorides. No published descriptions of this process have been found.

Production Trends. The amount of phosphate rock utilized as a feed to the defluorination process in 1970 was 87,700 tons (as P_2O_5)(4264). This corresponded to a per capita consumption of 0.84 pound (as P_2O_5). If this consumption level remains constant to the year 2000, there will be 141,200 tons of rock (as P_2O_5) utilized in the defluorination process.

Fluoride Emission Control Techniques. Since defluorination removes more than 95% of the incoming fluorine, the exhaust gas stream from the kiln or fluid bed reactor is quite concentrated in fluoride content. With the majority of fluorides present as hydrogen fluoride and silicon tetrafluoride,this gas stream is vented via induced draft to a wet scrubbing system. The high fluoride concentration results in highly corrosive conditions in the exhaust gas ducting and collection equipment. The evolved gaseous fluorides are removed by water scrubbing in multi-pass spray chambers and spray towers in series with high energy wet scrubbers. Efficiencies average 99.5% for the overall scrubbing system. Attainment of this high efficiency level requires good basic system design, and prompt periodic maintenance. A controlled process model is presented as Figure 3-41.

Fluoride Emissions. Fluoride evolution and emission values are shown in Table 3-52. In the processes used for defluorination of rock, essentially all of the input fluoride is volatilized. Highly effective collection/scrubbing systems are employed to minimize emissions and mitigate an obvious potential problem. It is also obvious that a small percentage decrease in scrubber efficiency would result in multiplication of the emission factors.

Evolution from the production of dicalcium phosphate is poorly defined and no firm data has been reported. Based on RRI experience, it is estimated that 1760 tons of soluble fluorides were emitted by phosphate rock



②
PHOSPHORIC ACID +NaCl
③
FLUE GAS
RAW MATERIAL STORAGE
①
GRINDING
KILN
CLINKER STORAGE
MILL
④
PRODUCT TO STORAGE OR SALE
FUEL OIL AND AIR

BASIS: 100 TONS/DAY
PRODUCT (39.9% P_2O_5)

PROCESS STREAMS-TONS/DAY

MATERIAL	STREAM NUMBER			
	1	2	3*	4
HF			4.4(g)$^{(C)}$	
CaF_2 (Equiv)	8.77(s)			.16(s)$^{(B)}$
Total Fluoride	8.77		4.41	.16
Total As F	4.27		4.19	.08
Phosphate Rock 38% P_2O_5	92(s)			
Phosphoric Acid (15% P_2O_5)		33(l)$^{(A)}$		
NaCl		3(l)$^{(A)}$		
Product				
P_2O_5				39.9(s)$^{(B)}$
CaO				50.2(s)
Na_2O				4.6(s)
Insolubles				5.2(s)
H_2O			33(g)	
Combustion Products (15% excess air)			92(g)(est)	
APPROX. TOTAL STREAM	101	36	129	100

* Gaseous effluent stream

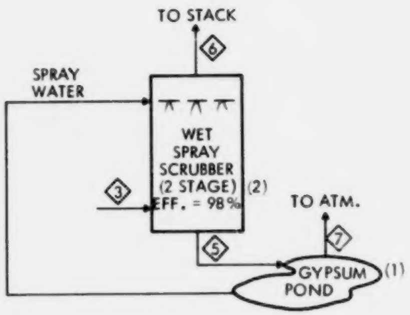
(A) Reference 5

(B) Reference 506

(C) Reference 4299

Soluble fluoride evolution factor = 210 lb F/ton P_2O_5 in product (240 lb F/ton P_2O_5 in phosphate rock fed.)

Figure 3-40. Defluorination of Phosphate Rock — Uncontrolled Process Model



(1) A FEW PLANTS LIME THEIR GYPSUM PONDS TO pH 4 TO DECREASE HF EVOLUTION.

(2) REFLECTS OPTIMUM OPERATING AND MAINTENANCE CONDITIONS

BASIS - 100 TONS/DAY OF PRODUCT (39.9% P_2O_5)

PROCESS STREAMS - TONS/DAY

Material	Stream Number			
	3	5	6*	7*
HF	4.41(g)$^{(B)}$	4.32(1)	0.09(g)$^{(C)}$	0.05(g)(Est)
Total Fluoride	4.41	4.32	0.09	0.05
Total as F	4.19	4.10	0.09	0.05
H_2O	33(g)	33(1)		
Hydrocarbon Combustion Products and N_2	92(g)(est)		92(g)	
Approx. Total Stream	129	37$^{(A)}$	92	0.05

* Gaseous Effluent Streams

(A) Plus 1.8 x 10^6 gal scrubbing water

(B) Reference 4299

(C) Reference 4267.

(D) Estimate average scrubber efficiency to be 90% with current maintainance and operation techniques and fugitive emissions equal to 5% of evolution.

Source	Soluble Fluoride Emission Factor lb F/Ton P_2O_5 in Product (assuming Optimum Conditions)	Soluble Fluoride Emission Factor lb F/Ton P_2O_5 in Product (assuming average Industry Operation)
Scrubber	4.5	21.0
Gypsum Pond Emission	2.5	2.5
Assumed Fugitive Emission	0	10.5
Total Soluble Fluoride Emission	7.0	34.0

Overall soluble fluoride emission facto· for defluorination of phosphate rock (including gypsum ponds) = 34 lb F/ton P_2O_5 in product (39 lb F/ton P_2O_5 in phosphate rock fed) (D)

Figure 3-41. Defluorination of Phosphate Rock — Controlled Process Model

defluorination in 1970, and that 2730 tons of soluble fluorides (as F) will be emitted in 2000. If 99% efficient control systems are employed, emission for 2000 will drop to 170 tons.

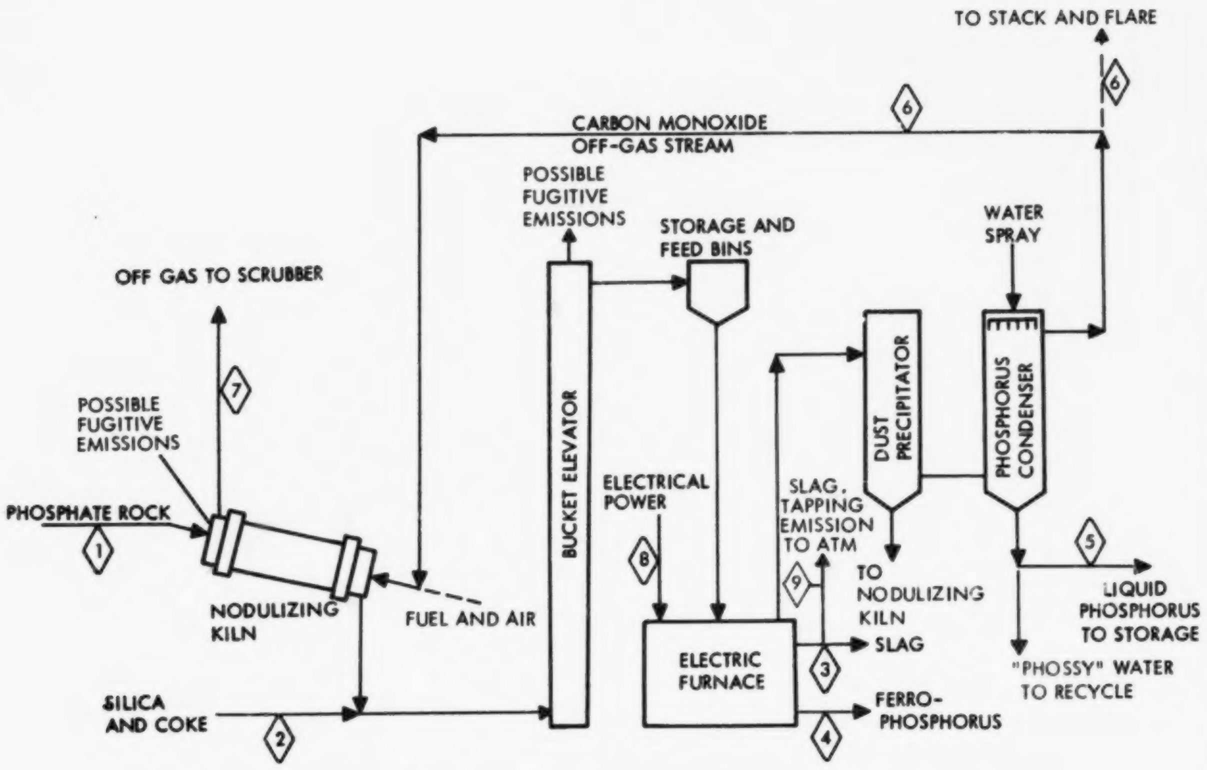
Table 3-52. Evolution and Emission of Fluoride From Defluorination of Phosphate Rock

Defluorination Processor	Evolution (pound fluoride/ton P_2O_5)	Emission (pound fluoride/ton P_2O_5)
Thermal		
Kiln	210	0.6
Fluid Bed	210	0.3
Chemical		
DiCal Reactor*	**	0.04

*defluorination of phosphoric acid
**not reported

3.5.5.6 Elemental Phosphorus Production

Industry Discussion. Elemental phosphorus is produced by electric furnace smelting of phosphate rock with silica and coke. A flow chart for a typical plant is shown in Figure 3-42. The phosphate rock is agglomerated by sintering or nodulizing and, with the proper proportions of silica and coke, fed to an electric furnace for smelting. The phosphorus produced is volatilized and evolved from the furnace in a gas stream consisting mainly of carbon monoxide. Particulates are removed using an electrostatic precipitator and recycled to the nodulizer, and the product phosphorus is condensed in a direct contact scrubber/condensor. Iron present in nearly all phosphatic rock is reduced to elemental iron which alloys with the phosphorus generated and constitutes a ferrophosphorus byproduct. The mineral constituents of the feed (calcium, silicon, etc.) form a molten slag layer. Details of the process are available in Reference 4244.


TO STACK AND FLARE
6
CARBON MONOXIDE
OFF-GAS STREAM
6
POSSIBLE
FUGITIVE
EMISSIONS
STORAGE AND
FEED BINS
WATER
SPRAY
OFF GAS TO SCRUBBER
7
POSSIBLE
FUGITIVE
EMISSIONS
BUCKET ELEVATOR
DUST
PRECIPITATOR
PHOSPHORUS
CONDENSER
ELECTRICAL
POWER
SLAG,
TAPPING
EMISSION
TO ATM
PHOSPHATE ROCK
1
8
9
TO
NODULIZING
KILN
5
LIQUID
PHOSPHORUS
TO STORAGE
NODULIZING
KILN
FUEL AND AIR
ELECTRIC
FURNACE
3
SLAG
"PHOSSY" WATER
TO RECYCLE
SILICA
AND COKE
2
4
FERRO-
PHOSPHORUS

NOTE: ALTERNATE METHOD OF PROCESS OPERATION SHOWN AS DOTTED LINES (-----)

Materials
SiF_4 (Equiv.) CaF_2 (Equiv.)
Total Fluoride Total as F
Phosphate Rock Silica (Gravel) Coke Electrical Power (Slag Ferro-Phosphorus CO CO_2 N_2 Phosphorus
Approximate Total Stream

* Gaseous Effluent

Soluble fluoride e

(A) Reference 4299
(B) Reference 426
(C) Reference 424
(D) Reference 426

A

BASIS: ELECTRIC FURNACE PRODUCTION OF 30 TONS PHOSPHORUS PER DAY

PROCESS STREAMS (Tons/Day)

erials	Stream Number								
	1	2	3	4	5	6	7*	8	9*
$_4$ (Equiv.) $_2$ (Equiv.)	18.3(s)$^{(B)}$		16.2(l)$^{(B)}$			0.003(g)$^{(A)}$	1.4(g)$^{(B)}$		0.03(g)$^{(A)}$
l Fluoride	18.3		16.2			0.003	1.4		0.03
l as F	8.9		7.9			0.002	1.0		0.02
sphate Rock	210(s)$^{(D)}$								
ica (Gravel)		70(s)$^{(D)}$							
		35(s)$^{(D)}$							
trical Power (KW)								15,000KW$^{(C)}$	
			270(l)$^{(B)}$						
o-Phosphorus				10(l)$^{(B)}$					
						80(g)$^{(B)}$			
							125(g)$^{Est.}$		
							80(g)$^{Est.}$		
phorus					30(l)$^{(C)}$				
ximate Total am	210	105	270	10	30	80	205	--	0.03

eous Effluent Stream

le fluoride evolution factor = 68 lb F/ton P produced (30 lb F/Ton P_2O_5 equiv. in phosphate rock fed)

Reference 4299

Reference 4264

Reference 4244

Reference 4263

Figure 3-42. Electrothermal Phosphorus Production — Uncontrolled Process Model

B

Production. In 1968, 1.57 million tons of phosphate rock (expressed as P_2O_5) were utilized in the production of electrothermal phosphorus(4394) for a per-capita consumption of 15.6 pounds per person. If the per-capita consumption is assumed constant to the year 2000, the annual utilization of phosphate rock in this process will be 2.62 million tons (as P_2O_5). The current emphasis on low and no-phosphate detergents could materially alter these projections.

Fluoride Emission Control Techniques. Emphasis is placed on control of F emissions from the feed preparation, condensor off-gas, and slag tapping operations. The exhaust gas from feed preparation (nodulizing, etc.) contains the major portion of fluorides evolved from phosphorus production. Substantial emphasis has been placed on controlling this source of pollutant. The rock pretreatment kilns are hooded and vented under induced draft to dust and fluoride control equipment. Cooling prior to fluoride control is mandatory due to the high temperature (2200° to 2600°F) of the pretreatment kiln.

Spray towers or wet cyclone collectors are the control devices most commonly applied to the kiln gas stream. A relatively high concentration of particulate material may also be present in the exhaust gas stream. This particulate material is often collected using an electrostatic precipitator prior to the application of gas scrubbers and returned to the feed preparation process. Efficiencies of 96 to 99% have been achieved using the wet scrubbers.

The process of condensing and removing the product phosphorus from the furnace gas also absorbs most of the fluoride evolved in the furnace operation. The water used in the condensing system is recycled and clarified to remove dissolved phosphorus. A small amount of fresh water is added to prevent the build-up of dissolved material.

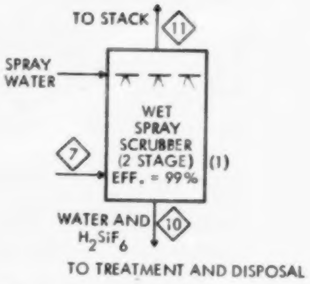
The gases released during the slag tapping and cooling operation are usually collected using a water cooled hood and ducted to wet scrubbers. Fluoride emissions from this source depend upon the method used to quench the slag after it is removed from the furnace. Water quenching generally produces approximately 6 times the amount of fluoride emissions as does air quenching of slag. In either case, the gas stream contains a low concentration of gaseous fluoride. The control devices predominantly used are simple water sprays or low pressure drop wet cyclones.

The attention given to the water pollution potential of the fluorides collected in scrubbing liquids has given rise recently to consideration of the use of fluorides recovered as by-product material from elemental phosphorus production. Recovery processes to produce such saleable by-products as cryolite and aluminum fluoride from scrubbing liquid fluorides have recently been described(506). Figure 3-43 presents a controlled process mass balance.

Fluoride Emissions. The fluorides introduced in the phosphate rock feed are evolved from three points in the process. These are feed preparation, condensor off-gas, and slag tapping. Volatilization of fluorides in the electric furnace itself is not considered to be a major emission source since the direct contact condensor will recapture most of the fluorides evolved. Table 3-53 shows the quantities of fluorides evolved and emitted from the three source points.

Feed preparation — drying, calcining, nodulizing, and cooling — is clearly the major element of total fluoride emission. Sintering and nodulizing of the rock feed requires heating to 2200 to 2600°F which results in evolution of fluorides. The emissions from feed preparation are listed as 5 to 59 pounds fluoride/ton of phosphorus since the degree of emission control and capture efficiency for emissions from feed preparation vary widely. Some facilities have no control and emissions will correspond to evolution. Reasonably efficient scrubbing should reduce fluoride emission by at least 90%, but feed preparation will still be the dominant emission component.

The off-gas from the phosphorus condensor has been processed to remove most of the particulate matter in the electrostatic precipitator and most of the phosphorus and gaseous fluoride in the condensor. The particulate matter is recycled to feed preparation. The condensor water is


TO STACK
11
SPRAY WATER
WET SPRAY SCRUBBER (2 STAGE) EFF. = 99%
(1)
7
WATER AND H_2SiF_6
10
TO TREATMENT AND DISPOSAL

(1) REFLECTS OPTIMUM OPERATING AND MAINTENANCE CONDITIONS

BASIS - 30 TONS/DAY PHOSPHORUS PRODUCTION

PROCESS STREAMS - TONS/DAY

Material	Stream Number			
	7	9*(E)	10	11*
SiF_4 Equiv.	1.4(g)(C)	0.03(g)(B)	1.39(D)	0.01(D)
Total Fluorides	1.4	0.03	1.39	0.01
Total as F	1.0	0.02	0.99	0.01
CO_2	125(g)			125(g)
N_2	80(g)			80(g)
Approx. Total Stream	205	0.03	1.39(A)	205

* Gaseous Effluent Stream

(A) Plus 128,000 gal scrubbing water

(B) Reference 4299

(C) Reference 4264

(D) Reference 4267

(E) Slag Tapping Emission

(F) Estimate average scrubber efficiency to be 90% with current maintainance and operation techniques and fugitive emissions equal to 5% of evolution.

Source	Soluble Fluoride Emission Factor - lb F/Ton P Produced (assuming optimum conditions)	Soluble Fluoride Emission Factor - lb F/Ton P Produced (assuming average Industry Operation)
Scrubber Effluent	0.7	6.8
Tapping Emission	1.3	1.3
Assumed Fugitive Emissions	0	3.4
Total Soluble Fluoride Emitted	2.0	11.5

Overall soluble fluoride emission factor = 11.5 lb F/Ton P produced(F)
(5.1 lb F/Ton P_2O_5 equiv in phosphate rock fed)

Figure 3-43. Electrothermal Phosphorus Production – Controlled Process Model

Table 3-53. Fluoride Evolution and Emission From Elemental Phosphorus

Process Element	Evolution Factor (pound fluorine/ ton phosphorus)	Emission Factor (pound fluorine/ ton phosphorus)
Feed Preparation	66.6	7 - 66.6
Condensor Off-Gas	0.1	0.1
Slag Tapping	1.3	1.3
Total	68	8 - 68

also recycled and may be treated to either recover fluoride values or prepare it for disposal. Pond emissions are discussed in Section 3.5.5.7. The off-gas is primarily carbon monoxide; it is typically either flared for disposal or burned for its heating value in the kiln. The fluoride evolution and emission factors for this gas are approximately 0.1 pounds fluorine/ton phosphorus.

Most of the fluoride entering the furnace exits in the slag. Slag is tapped periodically, and a small quantity of fluoride is evolved (about 1.3 pounds fluorine/ton phosphorus). A small minority of plants use a control system comprised of a hood over the tapping port and a scrubber on the duct.

Using the evolution factor of 68 pounds of fluoride per ton of phosphorus,(4157) and taking into account the efficiencies of current control techniques, soluble fluoride emissions for 1968 are estimated as 4080 tons (as F). If current techniques continue as means of control, soluble fluoride emissions for 2000 are projected as 6630 tons (as F). With the application of 99% efficient control systems emissions for 2000 would drop to 390 tons.

3.5.5.7 Gypsum Pond Emissions

In the manufacture of wet-process phosphoric acid, the washed gypsum filter cake with its entrapped acids and fluorides is reslurried with recycled water and transported via a flume to a gypsum pond for disposal. The various plant fluoride emission control scrubbers, which to a large extent use recycled water, similarly discharge to the gypsum pond. In an integrated plant, the wet emission control systems — for wet process H_3PO_4, triple superphosphate, ammonium phosphates, defluorinated phosphate rock — typically discharge to the gypsum pond. The pond is used for cooling, and for separation by settling of the solids, prior to reuse of the supernatant clarified overflow water. Some plants may use a separate pond for cooling and recirculation of process water.

Gypsum ponds have been observed to remain at a nearly constant fluoride content of 5000 to 10,000 ppm fluoride for months without dumping of water to disposal. It appears that an equilibrium exists between fluoride inputs from the processes and fluoride outputs by volatilization, precipitation, etc. The volatilization, which is of principal concern for this study, has been measured by Cross and Ross(323) to be a minimum of 0.16 pounds/acre-day for a 160-acre gypsum pond in a fertilizer complex producing sulfuric acid, DAP, TSP, and phosphoric acid (500 tons P_2O_5/day). The water system also included a 100-acre cooling pond, but emissions from it were not measured. An investigation pursuing similar goals was performed by Tatera(4300) who measured and correlated emissions from a model pond. For a water temperature of 85°F and a wind velocity of 5 miles per hour (7.3 feet/second), Tatera's emission values were 7 and 4.5 pound/acre-day for gypsum pond and process water ponds, respectively. Based on these factors and assuming the same ratio of pond area to P_2O_5 production as reported by Cross and Ross, the total annual fluoride emission from gypsum ponds is 4520 tons fluoride/year and from process water ponds is 1810 tons fluoride/year. The magnitude of the emission factor estimated from evaporation rates(4285) is consistent with the Tatera data, and the sizes and chemistry of the ponds for the reported Florida complex should be representative.

Emission control at or above the 99% level is readily attainable by "liming" the ponds - using sufficient lime or limestone to react with the soluble fluorides and acid. Currently, this represents the only practical process for pond emission control.

Table 3-54 presents estimates of soluble fluoride emissions for the phosphate rock processing industry. Total for 1970 is estimated at 6250 tons (as F); if current practice continues, the total for 2000 would drop to 210 tons.

It should be noted that an appropriate portion of the total soluble fluoride emissions from ponds has been allocated to each of the various processes utilizing the pond as shown in Table 3-54.

3.5.5.8 Other Phosphate Processes

Furnace Grade Phosphoric Acid. Furnace grade phosphoric acid is made from phosphate rock through the intermediate production of elemental phosphorous. The fluoride content of the rock is evolved in the manufacture of the phosphorus rather than in the manufacture of the acid. Evolution of fluoride in the manufacture of phosphorus is discussed in Section 3.5.5.6 and no appreciable further evolution of fluoride will occur in making furnace acid.

Superphosphoric Acid. Manufacturing processes for production of superphosphoric acid from wet phosphoric acid are essentially extensions of vacuum concentration process techniques to the 70 percent P_2O_5 level, and evolved fluorides are collected in barometric leg condenser water. Evolution of fluoride will occur from sumps and vents in the same manner as in the other vacuum concentration processes. Based on RRI experience, the evolution from sumps, vents, and tail gas in the superphosphoric acid process will amount to approximately 1 pound of soluble fluoride (as F) per ton of P_2O_5 produced. Scrubber efficiencies are at least 90%. Based on these values and the production rate of 600,000 tons P_2O_5 per year, the

Table 3-54. Gypsum Pond Emissions

	Wet Process Phosphoric Acid	Granulated Triple Superphosphate	Diammonium Phosphate	Defluorination of Phosphate Rock	Industry Total(E)
Soluble Fluoride Emission Factor(C)	3.14 lb F/ton P_2O_5 in Product	0.2 lb F/ton P_2O_5 in Product	0.009 lb F/ton P_2O_5 in Product	2.9 lb F/ton P_2O_5 in Phosphate Rock Feed	1.6 to 1.8 lb F/ton P_2O_5 in Product
1970 Production (10^6 tons/year)	3.8(B)	1.4(B)	2.4(B)	0.09(A)	7.7
Projected 2000 Production (10^6 tons/year)	13(B)	2.4(B)	7.0(B)	0.14(A)	22.9
Soluble Fluoride Emitted Currently (10^3 tons F/year)	5.97	0.14	0.011	0.13	6.25
Soluble Fluoride Emitted in 2000 with Currently Used Controls (10^3 tons F/year)	20.4	0.27	0.032	0.20	20.9(D)
Soluble Fluoride Emitted in 2000 with 99% control (10^3 tons F/year)	0.2	0.003	0.0003	0.002	0.21(D)

(A) Expressed as P_2O_5 equivalent in phosphate rock feed

(B) Expressed as P_2O_5 equivalent in product

(C) Assumes no lime addition to ponds and an emission equivalent to 0.013 lb F per lb. F feed to ponds

(D) Reflects change due to shifts in production trends through 2000

(E) Includes only processes which utilize ponds for disposal evolution and emission of fluoride from superphosphoric acid manufacture are 310 tons of soluble fluorides as fluorine per year and 31 tons per year, respectively.

Insoluble Dust Emissions. Evolution and emission of fluoride as insoluble dust is of less importance than gaseous emissions because of the lesser environmental effect produced. This difference results from the relatively inert character of the insoluble solid fluorides, and the tendency not to be transported out of the plant boundaries because of particle fallout. The majority of dust emissions can be expected to be phosphate rock since all rock undergoes size reduction, drying, and handling in fine particulate form while many products do not. Available data(4301) indicate emission rates of about 1 pound dust/ton of product for grinding and drying of rock. That is equivalent to 0.1 pound fluoride/ton P_2O_5 or a total annual emission of 410 tons fluoride/year.

3.5.6 Economic Analysis

3.5.6.1 Wet Process Phosphoric Acid

Basic Processes. The economic analyses for wet process phosphoric acid and the requisite captive sulfuric acid production are presented in Tables 3-55 and 3-56, respectively, for four typical plant sizes. If the equity funding requirements for the captive sulfuric acid plants are included in total equity funding requirements, return on investment for wet process phosphoric acid plants varies between 4.5% (for the 100 ton per day plant) and 44.0% (for the 1000 ton per day plant), assuming that all of the acid produced is sold as merchant 75% phosphoric acid. This is almost never the case. Most wet process H_3PO_4 plants sell only a small portion of their output as merchang H_3PO_4; the bulk of the H_3PO_4 produced is employed as captive acid in the manufactureof ammonium phosphates and simple superphosphate.

Table 3.55. Estimated Economics of Wet Process Phosphoric Acid Production (54% P_2O_5) (Excluding Pollution Control Costs)

	Plant Capacity (Tons P_2O_5)			
	100 ton/day	400 tons/day	700 tons/day	1000 tons/day
Capital Investment				
Installed Capital (A)	1.94 \$MM	4.70 \$MM	6.46 \$MM	8.34 \$MM
Off Sites	0.58	1.41	1.92	2.50
Total Capital Investment (A)	2.52	6.11	8.38	10.84
Total Capital Investment (D)	3.84	9.70	13.44	17.10
Production Costs				
Direct Costs				
Phosphate Rock (3.48 tons of 66 bpl/ton P_2O_5)	22.62\$/ton P_2O_5	22.62\$/ton P_2O_5	22.62/ton P_2O_5	22.62\$/ton P_2O_5
Sulfuric Acid (B) (2.56 tons 100% H_2SO_4/ton P_2O_5)	29.25	23.09	22.05	21.71
Water (from sulfuric acid plant)	0	0	0	0
Steam (from sulfuric acid plant)	0	0	0	0
Electric Power (250 kwh/ton P_2O_5)	1.75	1.75	1.75	1.75
Gypsum Disposal	0.50	0.50	0.50	0.50
Rock Grinding and Handling	3.62	3.62	3.62	3.62
Operating Labor (5 men per shift)	4.80	1.20	0.69	0.48
Supervision and Fringe Benefits	4.80	1.20	0.69	0.48
Maintenance and Supplies	4.58	2.78	2.18	1.97
Total Direct Costs	71.92	56.76	54.10	53.13
Indirect Costs				
Depreciation (at 10% per year) (A)	7.63	4.63	3.63	3.28
Interest (at 7%, 20% debt)	1.07	0.65	0.51	0.46
Taxes and Insurance	2.29	1.39	1.09	0.99
Plant and Labor Overhead	5.76	1.44	0.82	0.58
Total Indirect	16.75	8.11	6.05	5.31
Manufacturing Cost (\$/ton P_2O_5)	88.67	64.87	60.15	58.44
Manufacturing Cost (\$/ton 75% H_3PO_4)	48.17	35.24	32.67	31.75
General and Sales Expenses (\$/ton 75% H_3PO_4)	0.96	0.70	0.65	0.63
F.o.b Cost (\$/ton 75% H_3PO_4)	49.13	35.94	33.32	32.38
Product Revenue (\$/ton 75% H_3PO_4)	54.00	54.00	54.00	54.00
Profit After Taxes (taxes at 50%, \$/ton 75% H_3PO_4)	2.44	9.03	10.34	10.81 \$/ton
Cash Flow (\$MM/Year) (A)	0.40 \$MM/yr	2.81	5.23	7.71 \$mm/yr
Return on Investment (C) (D)	4.5%	25.9%	37.4%	44.0%

(A) Does not include sulfuric acid plant capital.
(b) Sulfuric acid plant is co-located with wet process phosphoric plant.
(C) Assumes 80% capacity funding equity funding for capital other than sulfuric acid plant, and 100% equality funding for sulphuric acid plant.
(D) Including sulfuric acid plant capital

Table 3-56. Estimated Economics of Sulfuric Acid Production(A) (Excluding Pollution Control Cost)

	Plant Capacity (Tons 100% H_2SO_4)			
Capital Investment	200 Tons/Day	600 Tons/Day	1200 Tons/Day	2000 Tons/Day
Installed Capital	0.85$MM	1.90$MM	3.06$MM	4.15$MM
Off Sites	0.26	0.57	0.92	1.25
Total Capital Investment	1.11$MM	2.47$MM	3.98$MM	5.40$MM
Production Costs				
Direct Costs				
Sulfur (0.3 long tons s/ton 100% H_2SO_4, S at $21/long ton)	6.36$/ton 100% H_2SO_4	6.36$/ton 100% H_2SO_4	6.36$/ton 100% H_2SO_4	6.36$/ton 100% H_2SO_4
Water (6 M-gallons/ton 100% H_2SO_4)	0.18	0.18	0.18	0.18
Electric Power (8kwh/ton 100% H_2SO_4	0.06	0.06	0.06	0.06
Operating Labor (2 men/shift)	0.96	0.32	0.16	0.10
Supervision and Fringe Benefits	0.96	0.32	0.16	0.10
Maintenance and Supplies	1.01	0.75	0.60	0.49
Total Direct Cost (B)	9.53	7.99	7.52	7.29
Indirect Costs				
Depreciation	1.68	1.25	1.01	0.82
Local Taxes and Insurance	0.50	0.37	0.30	0.25
Plant and Labor Overhead	1.15	0.38	0.19	0.12
Total Indirect Cost	3.33	2.00	1.50	1.19
Manufacturing Cost ($/Ton 100% H_2SO_4)	12.86	9.99	9.02	8.48

(A) Total H_2SO_4 production assumed to be captive to wet process H_3PO_4 usage in-house.

(B) Steam credit not included (valued at 1.1 tons of high pressure steam/ton 100% H_2sO_4).

Impact of Control. Analyses of the cost of fluoride emission control using each of the three processes currently employed by the industry are presented in Tables 3-57, 3-58, and 3-59. The decrease in ROI is nominal in each case.

3.5.6.2 Diammonium Phosphate

Basic Processes. Table 3-60 presents economic analyses of two typical sizes of DAP plant. ROI varies from 15.5% at the smaller plant size to 19.1% for the 1000 ton per day unit.

Impact of Control. Table 3-61 presents an analysis of the cost of fluoride emission control for DAP plants. ΔROI's are about -2%.

3.5.6.3 Triple Superphosphate

Basic Process. Table 3-62 presents the economics of production for granular triple superphosphate at the indicated sales price. ROI's for the four plant sizes chosen ranges from 6.0 to 18.0%.

Impact of Control. Table 3-63 presents the analyses of the cost of control of fluoride emissions from TSP manufacture, using current techniques. Change in Return on Investmend due to emission control for a 600 ton per day TSP plant is approximately 14%.

3.5.6.4 Normal Superphosphate

Basic Process. Table 3-64 presents an economic analysis of production costs and ROI's for three typical plant sizes. It should be noted that for plant sizes below 200 tons/day (and many of the older plants are in this range), operations fall below the break-even point and are profitable only if equipment has been fully depreciated.

Impact of Control. Tables 3-65 through 3-68 present emission control economics for continuous and batch NSP plants.

Table 3-57. Wet Process Phosphoric Acid - Estimated Economics of Control Process A Basis - 1000 Tons Per Day of Phosphoric Acid (P_2O_5 basis) Produced.

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	SPRAY SCRUBBER, 2 scrubbers, 8' diameter by 18', 2 in WG pressure drop, monel clad, 8 ft/sec allowable velocity, 70,000 scfm, 30 horsepower 3000 gpm, neoprene lined steel	47	4383 4391 4392	2.57		121
2	GYPSUM POND(16)	-	-	-		50
				Capital Subtotal		171
				Indirects (@ 15%)		26
				Contingency (@ 20%)		34
				Total Capital (as of January 1971)		231

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.16	0.50		0.66
2	-	0.38		0.38
Subtotal				1.04
Water(21) (3000 gpm, 90% recycle)				0.36
Disposal(22)				-
Total Operating Cost				1.40

Total Operating Cost ($/hr)	1.40
Taxes and Insurance (2%, 330 days)	0.58
Capital (9.1%, 330 working days)	2.65
Pollution Control Cost ($/hr)	4.63
Pollution Control Cost ($/ton)	0.11

Table 3-58. Wet Process Phosphoric Acid - Estimated Economics of Control Process B Basis - 1000 Tons Per Day of Phosphoric Acid (P_2O_5 basis) Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	VENTURI SCRUBBER, 85,000 cfm, 714 gpm, neoprene lined steel, 31.5 in W.G. pressure drop, 564 horsepower	112	4383 4390 4391	1.73		194
2	GYPSUM POND(17)	-	-	-		50
				Capital Subtotal		244
				Indirects (@ 15%)		37
				Contingency (@ 20%)		49
				Total Capital (as of January 1971)		330

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	2.94	0.13		3.07
2	-	0.38		0.38
Subtotal				3.45
Water(21) (714 gpm, 90% recycle)				0.09
Disposal(22)				-
Total Operating Cost				3.54

Total Operating Cost ($/hr)	3.54
Taxes and Insurance (2%, 330 days)	0.83
Capital (9.1%, 330 working days)	3.79
Pollution Control Cost ($/hr)	8.16
Pollution Control Cost ($/ton)	0.20

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Table 3-59. Wet Process Phosphoric Acid - Estimated Economics of Control Process C Basis - 1000 Tons Per Day of Phosphoric Acid (P_2O_5 basis) Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	SPRAY CROSS - FLOW PACKED SCRUBBER, 2 at 10'-6" X 10'x12', 2 in W.G. pressure drop, 85,000 cfm, neoprene lined steel, 8 ft/sec velocity, 30 hp	39	4383 4391 4392	2.56		100
2	GYPSUM POND(17)	-	-	-		50
				Capital Subtotal		150
				Indirects (@ 15%)		23
				Contingency (@ 20%)		30
				Total Capital (as of January 1971)		203

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.16	0.50		0.66
2	-	0.38		0.38
Subtotal				1.04
Water(21) (3000 gpm, 90% recycle)				0.36
Disposal(22)				-
Total Operating Cost				1.40

Total Operating Cost ($/hr)	1.40
Taxes and Insurance (2%, 330 days)	0.51
Capital (9.1%, 330 working days)	2.33
Pollution Control Cost ($/hr)	4.24
Pollution Control Cost ($/ton)	0.10

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Table 3-60. Estimated Economics of Diammonium Phosphate (18-46-0) Production (Excluding Pollution Control Cost)

	Plant Capacity	
	800 tons/day	1000 tons/day
Capital Investment		
Installed Capital	1.52 $MM	1.67 $MM
Off Sites	0.30	0.33
Total Invested Capital(A)	1.82	2.00
Production Costs		
Direct Costs		
Phosphoric Acid (0.87 tons 54% P_2O_5/ton)	31.40 $/Ton	30.39 $/Ton
Ammonia(B) (0.23 Tons/ton)	13.80	13.80
Electric Power (20 kwh/ton)	0.14	0.14
Fuel Oil (3 gallon/ton)	0.24	0.24
Operating Labor (2 men/shift)	0.25	0.20
Supervision and Fringe Benefits	0.25	0.20
Maintenance and Supplies	0.41	0.36
Total Direct Cost	46.49	45.33
Indirect Costs		
Depreciation	0.69	0.61
Interest (at 7%, 20% debt)	0.10	0.08
Taxes and Insurance	0.21	0.81
Plant and Labor Overhead	0.30	0.24
Total Indirect Cost	1.30	1.11
Manufacturing Cost	47.79	46.44
General and Sales Expenses	0.96	0.93
F.o.b Cost ($/ton)	48.75	47.37
Product Revenue ($/ton 18-46-0)	60.00	60.00
Profit After Taxes (at 50%, $/ton)	5.63	6.32
Cash Flow ($MM/year)	1.67 $MM/yr	2.28 $MM/yr
Return on Investment (C)	15.5%	19.1%

(A) Wet Process Phosphoric Acid Plant co-located.
(B) Assumes 95% recovery.
(C) Assumes 80% equity funding capital outlay for Wet Process Phosphorus acid plant not shown but allocated for calculating ROI.

Table 3-61. Diammonium Phosphate Production - Estimated Economics of Control Process Basis - 500 Tons Per Day of 18-46-0 Diammonium Phosphate Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	AMMONIA SCRUBBER, 3' diameter by 8', 2000 cfm, 2 in. W.G. pressure drop, neoprene lined steel	4	4387 4390 4391	2.50		10
2	TAIL GAS SPRAY SCRUBBER, (Cross flow), 6' by 2' by 4', 2000 cfm, W.G. pressure drop, neoprene lined	3	4387 4390 4391	3.00		9
3	DUST SCRUBBER, 3' diameter by 8', 1000 cfm, 2 in. W.G. pressure drop, neoprene lined steel	4	4387 4390 4391	2.50		10
4	RECYCLE TANK, 10,000 gal, neoprene lined steel	6	4383	2.50		15
					Capital Subtotal	44
					Indirects (@ 15%)	7
					Contingency (@ 20%)	9
					Total Capital (as of January 1971)	60

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.02	0.25		0.27
2	0.02	0.25		0.27
3	0.01	0.25		0.26
4	-	0.06		0.06
Subtotal				0.86
Water(21) (170 gpm, 90% recycle)				0.02
Disposal(22)				-
Total Operating Cost				0.88

Total Operating Cost ($/hr)	0.88
Taxes and Insurance (2%, 330 days)	0.15
Capital (9.1%, 330 working days)	0.69
Pollution Control Cost ($/hr)	1.72
Pollution Control Cost ($/ton)	0.08

Table 3-62. Estimated Economics of Granular Triple Superphosphate Production (0-46-0) (Excluding Pollution Control Cost)

	Plant Capacity			
	300 Tons/Day	600 Tons/Day	800 Tons/Day	1000 Tons/Day
Installed Capital	1.19 $MM	1.66 $MM	1.90 $MM	2.14 $MM
Off Site	0.24	0.33	0.38	0.43
Total Capital Investment	1.43	1.99	2.28	2.57
Production Costs				
Direct Costs				
Phosphoric Acid (0.648 tons 54% P_2O_5/ton (0-46-0)	22.83 $/Ton$^{(D)}$	22.83 $/Ton$^{(D)}$	21.17 $/Ton$^{(E)}$	21.17 $/Ton$^{(E)}$
Phosphate Rock (75 bpl at 0.393 tons/ton (0-46-0)	4.01	4.01	4.01	4.01
Electrical Power (7 Kwh/ton at 0.007 $/Kwh)	0.05	0.05	0.05	0.05
Fuel Oil (3 gal/ton)	0.18	0.18	0.18	0.18
Rocking Grinding and Handling	0.68	0.68	0.68	0.68
Operating Labor (2 men per shift)	0.68	0.34	0.25	0.20
Maintenance and Supplies	0.87	0.60	0.52	0.47
Total Direct Costs	29.98	29.03	27.11	26.96
Indirect Costs				
Depreciation	1.44	1.01	0.86	0.78
Interest (at 7%, 20% debt)	0.20	0.14	0.12	0.11
Taxes and Insurance	0.44	0.30	0.26	0.24
Plant and Labor Overhead	0.82	0.41	0.30	0.24
Total Indirect	2.90	1.86	1.54	1.37
Manufacturing Cost (A)	32.88	30.89	28.65	28.33
General and Sales Expenses	0.66	0.62	50.57	0.57
F.o.b. Cost	33.54	31.51	29.22	28.90
Product Revenue	38.00	38.00	38.00	38.00
Profit after Taxes (at 50%)	2.23 $/Ton	3.25 $/Ton	4.39 $/Ton	4.55 $/Ton
Cash Flow	0.36 $MM/Yr.	0.84 $MM/Yr.	1.39 $MM/Yr.	1.76 $MM/Yr.
Return on Investment$^{(B,C)}$(%)	6%	10%	16.6%	17.8%

(A) A pulverized superphosphate plate (for use in ammoniated fertilizers) requires an initial capital investment approximately equal to that of a Granular triple superphosphate plant of equal capacity. This cost differential (approximately 2.50 $/Ton) is considerably reduced when local air pollution regulations require an extensive gas scrubbing system due to the increased cost of "clearing up" a granular plant.
(B) Includes capital for wet process phosphoric acid facility—co located.
(C) Assumes 80% equity funding.
(D) Based on H_3PO_4 manufacturing cost for 400 NT (P_2O_5)/day wet process H_3PO_4 plant.
(E) Based on H_3PO_4 manufacturing cost for 700 NT (P_2O_5)/day wet process H_3PO_4 plant.

Table 3-63. Granulated Triple Super Phosphate - Estimated Economics of Control Process Basis - 200 Tons Per Day of Triple Superphosphate (48% P_2O_5) Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	CYCLONIC SPRAY TOWER, 23,000 cfm, 8 ft/sec allowable velocity, 4 ft diameter by 10 ft, neoprene lined steel, 3 in W.G. pressure drop, 15 hp	20	4386 4383 4387	2.15		43
2	GYPSUM POND(16)	-	-	-		50
3	SPRAY SCRUBBER, 20,000 cfm, 8 ft/sec allowable velocity, 2 at 4 ft diameter by 8 ft, neoprene lined steel, 2 in W.G. pressure drop, 17 hp	18	4387 4390 4391	2.55		46
	Capital Subtotal					139
	Indirects (@ 15%)					21
	Contingency (@ 20%)					28
	Total Capital (as of January 1971)					188

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.08	0.13		0.21
2	-	0.38		0.38
3	0.09	0.25		0.34
Subtotal				0.93
Water(21) (645 gpm, 90% recycle)				0.08
Disposal(22)				-
Total Operating Cost				1.01

Total Operating Cost ($/hr)	1.01
Taxes and Insurance (2%, 330 days)	0.47
Capital (9.1%, 330 working days)	2.16
Pollution Control Cost ($/hr)	3.64
Pollution Control Cost ($/ton)	0.44

Table 3-64. Estimated Economics of Normal Superphosphate (0-20-0) — Continuous Production (Excluding Pollution Control Cost)

	Plant Capacity		
	200 Tons/Day	350 Tons/Day	500 Tons/Day
Capital Investments			
Installed Capital	0.48 $MM	0.68 $MM	0.87 $MM
Off Sites	0.14	0.20	0.26
Total Capital Investment	0.62	0.88	1.13
Production Costs			
Direct Cost			
Phosphate rock[a] (75 bpl, 0.60 tons/ton product)	5.94 $/Ton Product	5.94 $/Ton Product	5.94 $/Ton Product
Sulfuric Acid (0.357 tons 100% H_2SO_4/ton product)	4.60	4.60	4.60
Electric Power (20.8 kwh/ton product)	0.15	0.15	0.15
Operating Labor (2 men/shift)	0.96	0.55	0.38
Supervision and fringe benefits	0.96	0.55	0.38
Maintenance and Supplies	0.74	0.60	0.54
Total Direct	13.35	12.39	11.99
Indirect Costs			
Depreciation (7.5 year, straight line)	1.24	1.01	0.91
Interest (at 7%, 20% debt)	0.13	0.11	0.10
Taxes and Insurance	0.37	0.30	0.27
Plant and Labor Overhead	1.15	0.66	0.46
Total Indirect	2.89	2.08	1.74
Manufacturing Cost ($/ton product)	16.24	14.47	13.73
General and Sales Expenses ($/ton product)	0.32	0.29	0.27
F.o.b. Cost ($/ton product)	16.56	14.76	14.00
Product Revenue ($/ton product)	17.00	17.00	17.00
Profit after Taxes (Taxes at 50%)	0.22	1.12	1.50
Cash Flow ($/year)	0.10	0.25	0.40 $MM
Return on Investment[b]	2.9%	18.4%	27.4%

[a] Includes $0.54/ton grinding

[b] Assumes 80% equity funding

Table 3-65. Continuous Normal Super Phosphate Production - Estimated Economics of Control Process A Basis - 200 Tons Per Day of Normal Superphosphate (20% P_2O_5) Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	VENTURI SCRUBBER - SEPARATOR TANK, 2 at 35,500 cfm, 300 gpm, neoprene lined steel, 33 in. W.G. pressure drop.	142	4386 4387 4390 4383	1.72		244
	Capital Subtotal					244
	Indirects (@ 15%)					37
	Contingency (@ 20%)					49
	Total Capital (as of January 1971)					330

Operating Cost ($1/hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	2.58	0.25		2.83
Subtotal				2.83
Water[21] (300 gpm, 90% recycle)				0.04
Disposal[22]				-
Total Operating Cost				2.87

Total Operating Cost ($/hr)	2.87
Taxes and Insurance (2%, 330 days)	0.83
Capital (9.1%, 330 working days)	3.79
Pollution Control Cost ($/hr)	7.49
Pollution Control Cost ($/ton)	0.90

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Table 3-66. Continuous Normal Superphosphate Production - Estimated Economics of Control Process B Basis - 200 Tons Per Day of Normal Superphosphate (20% P_2O_5) Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	CYCLONIC SEPARATORS, 2 at 140 gpm, 35,500 cfm, 5 in. W.G. pressure drop, neoprene lined steel	58	4383	2.60		151
					Capital Subtotal	151
					Indirects (@ 15%)	23
					Contingency (@ 20%)	30
					Total Capital (as of January 1971)	204

Operating Cost ($1/hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.40	0.25		0.65
Subtotal				0.65
Water(21) (140 gpm, 90% recycle)				0.02
Disposal(22)				-
Total Operating Cost				0.67

Total Operating Cost ($/hr)	0.67
Taxes and Insurance (2%, 330 days)	0.52
Caoital (9.1%, 330 working days)	2.34
Pollution Control Cost ($/hr)	3.51
Pollution Control Cost ($/ton)	0.42

* All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Table 3-67. Batch Normal Superphosphate Production - Estimated Economics of Control Process A Basis - 40 Tons Per Batch (1 batch per hour) of Normal Superphosphate (20% P_2O_5) Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	VENTURI SCRUBBER - SEPARATOR TANK, 2 at 70,000 cfm, 300 gpm, neoprene lined steel, 33 in. W.G. pressure drop.	238	4386 4387 4390 4383	1.73		412

Capital Subtotal	412
Indirects (@ 15%)	63
Contingency (@ 20%)	82
Total Capital (as of January 1971)	557

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($1/hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	5.15	0.25		5.40

Subtotal	5.40
Water[21] (300 gpm, 90% recycle)	0.04
Disposal[22]	-
Total Operating Cost	5.44

Total Operating Cost ($/hr)	5.44
Taxes and Insurance (2%, 330 days)	1.41
Capital (9.1%, 330 working days)	6.40
Pollution Control Cost ($/hr)	13.25
Pollution Control Cost ($/ton)	0.33

Table 3-68. Batch Normal Superphosphate Production - Estimated Economics of Control Process B
Basis - 40 Tons Per Batch (1 batch per hour) of Normal Superphosphate (20% P_2O_5) Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	CYCLONIC SEPARATORS, 2 at 140 gpm, 70,000 cfm, 5 in. W.G. pressure drop, neoprene lined steel.	88	4323	2.42		213
					Capital Subtotal	213
					Indirects (@ 15%)	32
					Contingency (@ 20%)	43
					Total Capital (as of January 1971)	288

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($1/hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.78	0.25		1.03
Subtotal				1.03
Water[21] (140 gpm, 90% recycle)				0.02
Disposal[22]				-
Total Operating Cost				1.05

Total Operating Cost ($/hr)	1.05
Taxes and Insurance (2%, 330 days)	0.73
Capital (9.1%, 330 working days)	3.31
Pollution Control Cost ($/hr)	5.09
Pollution Control Cost ($/ton)	0.13

3.5.6.5 Defluorination of Phosphate Rock

Basic Process. Table 3-69 presents the analysis of production costs and investment requirements for the defluorination of phosphate rock. Return on investment is estimated as 24.0%.

Impact of Control. Table 3-70 presents an analysis of the costs of currently employed fluoride emission control techniques. Impact on ROI (△ROI) is estimated as -7%.

3.5.6.6 Elemental Phosphorus

Basic Process. Table 3-71 presents the analyses of the costs and returns on investment (excluding pollution control costs) for integrated "white" phosphoric acid - elemental phosphorus plants at four levels of production - 100, 250, 450 and 600 tons of P_2O_5 per day. Return on investment ranges from 18.6 to 50.7%.

Impact of Control. Costs of control of emissions from elemental phosphorus plants are presented in Table 3-72. Impact on ROI is minimal.

Table 3-69. Estimated Economics of Defluorinated Phosphate Rock Production (Pollution Control Cost Excluded)

	PLANT CAPACITY	
	100 Tons Product/Day	
Total Capital Investment	2.2	$MM
Production Costs		
Direct Costs		
Phosphate Rock (75 b.p.l., 0.92 tons/ton product @ $9.20/ton)	8.46	$/net ton product
Phosphoric Acid (0.33 tons 15% P_2O_5/ton product @ $15.00/ton)	4.95	
Sodium Chloride (0.03 tons/ton product @ $28.60/ton)	0.86	
Fuel Oil (8 gallon/ton product @ $0.10/gallon)	0.80	
Labor (4 positions @ $4.00/hr)	3.84	
Fringe Benefits and Supervision	3.84	
Maintenance and supplies @ 6%)	4.00	
Total Direct Costs	26.75	
Indirect Costs		
Depreciation (@10%)	6.67	
Interest (at 7%, 20% debt)	0.93	
Local Taxes and Insurance (@3%)	2.00	
Plant and Labor Overhead	4.61	
Total Indirect Costs	14.21	
Total Average Costs ($/net ton product)	40.96	$/net ton
General and Sales Expenses ($/net ton product)	0.82	$/net ton
F.o.b. Cost ($/net ton product)	41.78	$/net ton
Average Product Revenue ($/net ton product)	70.00	$/net ton
Average Profit after Taxes (@ 50%)	14.11	$/net ton
Cash Flow ($MM/yr)	0.64	MM$/yr
Return on Investment (%)(a)	24.0%	

(a) Assumes 80% equity funding

Table 3-70. Defluorination of Phosphate Rock - Estimated Economics of Control Process Basis - 100 Tons Per Day of Product (39% P_2O_5)

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	SPRAY SCRUBBER, 2 STAGES 4 ft diameter by 10 ft, monel clad, 10,000 cfm, 8 ft/sec allowable velocity, 6 lb HF(g)/min, 2 in. W.G. pressure drop, 4 horsepower	13.	4383 4391 4392	1.77		23.
2	GYPSUM POND(17)	--	--	--		50.
					Capital Subtotal	73
					Indirects (@ 15%)	11
					Contingency (@ 20%)	15
					Total Capital (as of January 1971)	99

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1.	0.02	0.25		0.27
2.	--	0.38		0.38
Subtotal				0.65
Water(21) (217 gram, 90% recycle)				0.03
Disposal(22)				--
Total Operating Cost				0.68

Total Operating Cost ($/hr)	0.68
Taxes and Insurance (2%, 300 days)	0.28
Capital (6.7%, 300 working days)	0.92
Pollution Control Cost ($/hr)	1.88
Pollution Control Cost ($/ton)	0.45

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Table 3-71. Estimated Economics of Phosphoric Acid Production by Electric Furnace (Pollution Control Costs Excluded)

	Plant Capacity (Tons P_2O_5)			
	100 Tons/Day	250 Tons/Day	450 Tons/Day	600 Tons/Day
Capital Investment				
Installed Capital$^{(A)}$	4.70 $MM	11.04 $MM	18.21 $MM	23.50 $MM
Off Sites	0.94	2.21	3.64	4.70
Total Capital Investment	5.64	13.25	21.85	28.20
Production Costs				
Direct Costs				
Phosphate Rock (66 bpl 3.82$^{(B)}$tons/ton P_2O_5)	24.83 $/Ton P_2O_5	24.83 $/Ton P_2O_5	24.83 $/Ton P_2O_5	24.83 $/Ton P_2O_5
Silica (Gravel at 1.27 tons/ton P_2O_5)	3.81	3.81	3.81	3.81
Coke$^{(C)}$ (0.60 tons/ton P_2O_5)	15.00	15.00	15.00	15.00
Lime (0.0133 tons/ton P_2O_5)	0.23	0.23	0.23	0.23
Water (31 M-gal/ton P_2O_5)	1.55	1.55	1.55	1.55
Electric Power (6220 kwh/ton P_2O_5)	43.54	43.54	43.54	43.54
Steam (2.75 M-lbs/ton P_2O_5)	1.90	1.90	1.90	1.90
Electrodes (13 lbs/ton P_2O_5)	3.25	3.25	3.25	3.25
Fuel Oil (50 gal/ton P_2O_5)	3.00	3.00	3.00	3.00
Operating Labor (22 men per shift)	21.12	8.45	4.69	3.52
Maintenance and Supplies	10.25	9.64	8.83	8.55
Supervision and Fringe Benefits	21.12	8.45	4.69	3.52
Total Direct Costs	149.60	123.65	115.32	112.68

Table 3-71. Estimated Economics of Phosphoric Acid Production by Electric Furnace (Continued)

	Plant Capacity (Tons P_2O_5)			
	100 Tons/Day	250 Tons/Day	450 Tons/Day	600 Tons/Day
Indirect Costs				
Depreciation	17.09	16.06	14.71	14.24
Interest (at 7%, 20% debt)	2.39	2.25	2.06	1.99
Taxes and Insurance	5.13	4.82	4.42	4.28
Plant and Labor Overhead	26.88	10.74	5.98	4.48
Total Indirect	51.44	33.87	27.17	24.99
Manufacturing Cost (\$/ton P_2O_5)	201.09	157.52	142.49	137.67
General and Sales Expenses (\$/ton P_2O_5)	4.02	3.15	2.85	2.75
F.o.b. Cost (\$/ton P_2O_5)	205.11	160.67	145.34	140.42
Product Revenue (\$/ton P_2O_5)(D)	256.00	256.00	256.00	256.00
Profit After Taxes (taxes at 50%, \$/ton P_2O_5)	25.45 \$/ton P_2O_5	47.67 \$/ton P_2O_5	55.33 \$/ton P_2O_5	57.79 \$/ton P_2O_5
Cash Flow (\$MM/yr)	1.40 \$MM/yr	5.26 \$MM/yr	10.40 \$MM/yr	14.26 \$MM/yr
Return on Investment(E)	18.6%	37.1%	47.1%	50.7%

(A) 100 Tons P_2O_5/Day plant requires a single 25,000 kva furnace; the 250, 450 and 600 tons P_2O_5/Day plants require multiple furnace units Of 50,000 kva.

(B) Assuming 90% overall recovery

(C) Assumes 86% fixed carbon, at \$15.00 per ton FOB, plus \$10.00 per ton freight.

(D) Revenue calculated by assuming a value of 139 \$/ton 75% H_3PO4 commercial grade acid.

(E) Assumes 80% equity funding

Table 3-72. Electrothermal Phosphorus Production - Estimated Economics of Control Process
Basis - 30 Tons of Phosphorus Produced Per Day

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	SPRAY SCRUBBER, 5'6" diameter by 13', 90 gpm water, monel clad, 5000 cfm, 2 in. W.G. pressure drop	20	4387 4390 4391	1.77		36
					Capital Subtotal	36
					Indirects (@ 15%)	5
					Contingency (@ 20%)	7
					Total Capital (as of January 1971)	48

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.02	0.25		0.27
Subtotal				0.27
Water$^{(21)}$ (90 gal min, 90% recycle)				0.02
Disposal$^{(22)}$				–
Total Operating Cost				0.29

Total Operating Cost ($/hr)	0.29
Taxes and Insurance (2%, 330 days)	0.12
Capital (9.1%, 330 working days)	0.55
Pollution Control Cost ($/hr)	0.96
Pollution Control Cost ($/ton)	0.77

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

3.6 GLASS MANUFACTURE

3.6.1 General

The glasses are manufactured by melting sand, limestone, soda ash and cullet (broken glass scrap) in a furnace. Minor constituents are added such as fining, oxidizing, coloring, and bleaching agents. Variations in the feed materials and compositions enable production of hundreds of product glasses, tailored to specific uses. One variety--soda-lime glass--accounts for 90% of U.S. production.

Because of the opacity in product glass caused by the presence of fluorspar (CaF_2) as a component or impurity in the furnace feed, CaF_2 has been minimized as a component in soda-lime glass for containers and in most other glass compositions. Only one glass composition--opal glass--makes deliberate use of fluorspar as a feed material in order to produce a translucent glass. The manufacture of opal glass is the major glass industry source of fluoride evolution and emission in the U.S.

3.6.2 Industry Description

Large direct fired furnaces are used for the continuous production of glass. Figure 3-43 contains a flow diagram and mass balance for a typical 60-ton-per-day, continuous-production opal glass furnace. Since fluoride evolution takes place only while the glass is molten, the portion of the plant involved in the manufacture of finished glass products is not shown.

Fluorides are evolved from the glass furnace as both gaseous and particulate species. Over half of the fluoride charge is volatilized as soluble fluorides, i.e., gaseous HF, solid and gaseous NaF, and gaseous BOF.

3.6.3 Production Trends

There are currently in the U.S. five major furnace installations producing opal glass; their individual capacities range from 60 to 70 tons per day. No estimates of future production are currently available. Since there are numerous types of opal glass with varying fluoride contents, predictions are based on the amount of fluorspar consumed for manufacture of opal glass.

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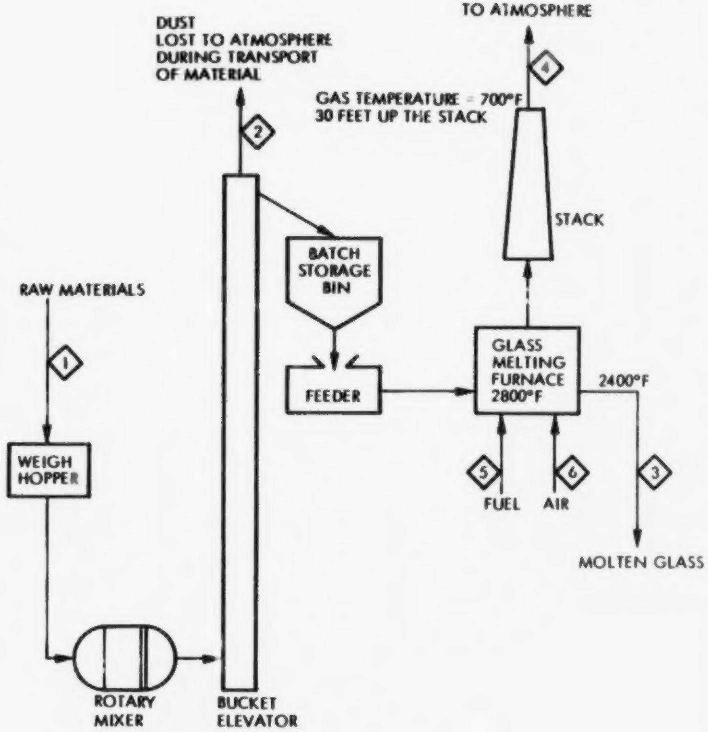

DUST
LOST TO ATMOSPHERE
DURING TRANSPORT
OF MATERIAL
TO ATMOSPHERE
GAS TEMPERATURE = 700°F
30 FEET UP THE STACK
RAW MATERIALS
1
WEIGH HOPPER
ROTARY MIXER
BUCKET ELEVATOR
2
BATCH STORAGE BIN
FEEDER
4
STACK
GLASS MELTING FURNACE 2800°F
2400°F
5
FUEL
6
AIR
3
MOLTEN GLASS

BASIS - 60 TONS/DAY OF OPAL GLASS PRODUCTION
PROCESS STREAMS - LB/HR

Material	Stream Numbers					
	1	2*	3	4*	5	6
HF				54 (g)$^{(C)}$		
CaF_2	560(s)$^{(A,B)}$	3 (s)$^{(C)}$	447(l)$^{(B)}$			
NaF				0.6(s)$^{(C)}$		
Total Fluorides	560	3	447	55		
Total as F	273	1.5	218	54		
SiO_2	2850	15	2840			
Al_2O_3	450	2.4	450			
B_2O_3	45	0.2	45			
Na_2CO_3	525	2.9		4.5(s)$^{(D)}$		
K_2O	90	0.5	90			
$CaCO_3$	450	2.3				
ZnO	420	2.3	420			
H_2O	90			1350 (g)		
CaO			240			
Na_2O			320			
N_2				10800 (g)		
O_2				1200 (g)		
CO_2				1950 (g)		
NO				30 (g)		
Natural Gas					530	
Air (50% R.H.)						14300
Approx Total	5480	29	4950	15000	530	14300

*Gaseous effluent Stream
Soluble fluoride evolution factor = 21.8 lb F/ton opal glass (193 lb F/ton CaF_2 fed)
(A) Reference 4251
(B) Reference 4255
(C) Reference 889
(D) Reference 4244

Figure 3-43. Opal Glass Production — Uncontrolled Process Model

The amount of fluorspar consumed in opal glass production will increase from about 35,000 tons in 1968(4291) to about 57,000 tons in 2000 (assuming a constant per-capita consumption of 0.34 pound--1968 value). Table 3-73 gives current and projected estimates of the amount of fluorspar used in opal glass production.

Table 3-73. Opal Glass Production

	1967	1968	Estimated(C) to Year 2000
Fluorspar Used in Glass(A) Production (tons)	31,800(4278)	34,500(4278)	57,200
U.S. Population (million)	199.1	202.3	336.2(B)
Per-Capita Consumption of Fluorspar Used in Glass(A) (pounds)	0.32	0.34	0.34

(A) Assumed to be opal glass.

(B) Based on estimated 1.6% annual growth rate.

(C) Based on per-capita consumption.

3.6.4 Fluoride Emission Control Techniques

As noted earlier, baghouse control techniques suitable for abatement of particulate dispersoid and fume from melting operations are the control devices currently employed in the opal glass industry. These devices are designed for use with the large, direct-fired continuous production glass furnaces.

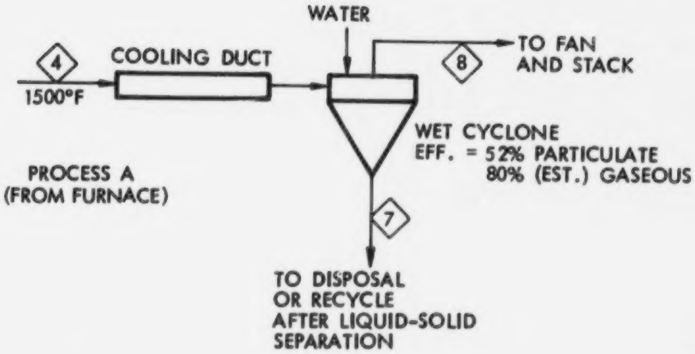
A summary of information on glass manufacturing and pollution control is contained in Reference 5156.

Figure 3-44 presents flow diagrams and mass balances for the three control processes currently employed, applied to abatement of effluent from a 60-ton-per-day opal glass plant. It should be noted that only Process A (the wet cyclone process) affords any control of soluble fluoride emissions, and that this process is used to a very minor extent--estimated at less than 1% of industry capacity.

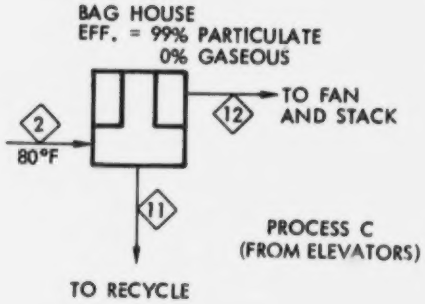
3.6.5 Fluoride Emissions

Relatively few data points on fluoride emissions from glass plants are available in the literature. Weyl(4258) reports that about 20% of the feed fluorspar is emitted. Substantiating this value, TRW-RRI experience indicates emissions which range as high as 17 pounds of fluorine per ton of glass produced, equivalent to 25% to 30% of the feed fluorspar for the glass compositions tested.

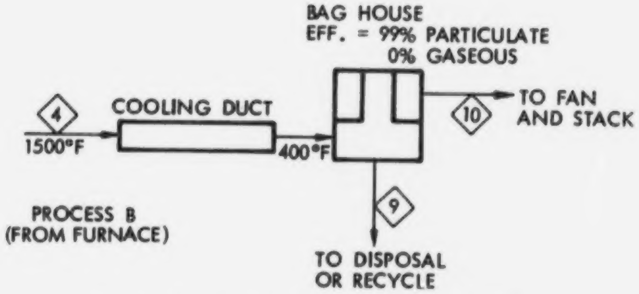
To verify the above data prior to the estimation of evolution and emission factors for opal glass manufacture, the proprietary thermochemical analysis program described in Section 3.1.2 was employed on a typical opal glass charge composition. At a system temperature of 2800°F (the normal glass furnace temperature), if equilibrium conditions were attained in the gas phase, 51.67% of the charged fluoride would be volatilized (Table 3-74). Almost all of the volatized fluorides would be soluble fluorides. Gaseous HF would be formed in major quantities from the reaction which takes place at high temperatures between gaseous CaF_2 and any gaseous source of hydrogen (including the water formed by combustion).



WATER
4
COOLING DUCT
1500°F
8
TO FAN AND STACK
WET CYCLONE
EFF. = 52% PARTICULATE
80% (EST.) GASEOUS
PROCESS A
(FROM FURNACE)
7
TO DISPOSAL OR RECYCLE AFTER LIQUID-SOLID SEPARATION



BAG HOUSE
EFF. = 99% PARTICULATE
0% GASEOUS
2
80°F
12
TO FAN AND STACK
11
TO RECYCLE
PROCESS C
(FROM ELEVATORS)



BAG HOUSE
EFF. = 99% PARTICULATE
0% GASEOUS
4
COOLING DUCT
1500°F
400°F
10
TO FAN AND STACK
PROCESS B
(FROM FURNACE)
9
TO DISPOSAL OR RECYCLE

NOTE: ASSUMES NO FLUORIDE ADSORPTION ON PARTICULATE MATTER

Material
HF
CaF_2
NaF
Total Fluorides
Total as F
SiO_2
Al_2O_3
B_2O_3
Na_2CO_3
K_2O
$CaCO_3$
ZnO
H_2O
N_2
O_2
CO_2
NO
Approx. Total Stream

*Gaseous Effluen

(A)Plus scrubbi

(B)Plus dilutio

(C)Utilization e

(D)Reference 51

S
Glass F
Bucket E
Total S Fluorid

Overall

A

BASIS - 60 TONS/DAY OF OPAL GLASS PRODUCTION PROCESS STREAMS - LB/HR
PROCESS STREAMS - LB/HR

Material	Stream Number							
	2	4	7	8*	9	10*	11	12*
HF		54(g)	43(1)	11(g)(D)		54(g)(D)		
CaF_2	3(s)						3(s)(D)	0.03(s)(D)
NaF		0.6(s)	0.3(s)(D)	0.3(s)(D)	0.6(s)(D)	0.006(s)		
Total Fluorides	3	55	43	11	0.6	54	3	0.03
Total as F	1.5	54	41	11	0.3	51	1.5	0.015
SiO_2	15(s)						15(s)	0.15(s)
Al_2O_3	2.4(s)						2.4(s)	0.03(s)
B_2O_3	0.2(s)						0.1(s)	0.002(s)
Na_2CO_3	2.9(s)	4.5(s)	2.4(s)	2.1(s)(D)	4.5(s)	0.04(s)(D)	2.8(s)	0.03(s)
K_2O	0.5(s)						0.5(s)	0.05(s)
$CaCO_3$	2.3(s)						2.2(s)	0.03(s)
ZnO	2.3(s)						2.2(s)	0.03(s)
H_2O		1350(g)	900(1)	4502(g)		1350(g)		
N_2		10800(g)		10800(g)		10800(g)		
O_2		1200(g)		1200(g)		1200(g)		
CO_2		1950(g)		1950(g)		1950(g)		
NO		30(g)		30(g)		30(g)		
Approx. Total Stream	29(B)	15000	900	14100	5	15000	30	0.3(B)

*Gaseous Effluent Stream

(A) Plus scrubbing water and recycled soluble fluorides.

(B) Plus dilution air.

(C) Utilization of soluble fluoride controlling processes (Process A) estimated to be less than 1%.

(D) Reference 5156

Source	Soluble Fluoride Emission Factor lb F/ton glass		
	Process A	Process B	Process C
Glass Furnace	4.4	21.8	-
Bucket Elevator	-	-	0
Total Soluble Fluoride Emission	4.4	21.8	0

Overall soluble fluoride emission factor for the industry = 21.8 lb F/ton opal glass (193 lb F/ton CaF_2 fed)

Figure 3-44. Opal Glass Production – Controlled Process Model

B

Table 3-74. Opal Glass Equilibrium Analysis Charge Composition (Includes Combustion Gas Charge)

	Weight, %	Mole, %
SiO_2	9.75	5.148
Al_2O_3	1.62	0.504
B_2O_3	0.17	0.076
Na_2CO_3	2.60	0.777
K_2O	0.32	0.108
$CaCO_3$	1.46	0.463
ZnO	1.46	0.568
CaF_2	1.615	0.913
CH_4	2.20	4.361
C_2H_6	0.74	0.783
N_2	59.30	67.172
CO_2	0.04	0.029
O_2	18.02	17.860
H_2O	0.70	1.234

Fluoride Distribution at 2800F

Product Compound	Concentration in Gas	% of Total Fluoride Charged
CaF_2	Condensed (liquid)	47.58
NaF	Condensed (liquid)	0.74
HF	9442.8 ppm	48.51
NaF	451.6 ppm	2.32
BOF	88.4 ppm	0.45
CaF_2	38.0 ppm	0.39

On the basis of the thermochemical analyses program results and private and open literature reports, an emission factor of 21.8 pounds of soluble fluorides per ton of opal glass product was chosen as a typical value. This emission factor corresponds to the emission of 20% of the charged fluorspar, in the form of soluble fluorides.

The opal glass industry emitted 3300 tons of soluble fluorides in 1968. Baghouse control used for dust abatement affords essentially no control of soluble fluoride emissions. If the baghouse control techniques currently employed are maintained through 2000, soluble fluoride emissions will rise to 5500 tons per year. If wet scrubbing techniques are employed to effect 99% abatement, soluble fluoride emissions in 2000 would be 55 tons per year. Table 3-75 summarizes soluble fluoride emission data for opal glass.

3.6.6 Economic Analysis

Basic Process

Table 3-76 presents the estimated economics for producing opal glass at two plant sizes characteristic of current production practice. Labor rates and material costs are typical of Gulf Coast data. Return on investment prior to use of fluoride control processes is estimated to be 14.5% and 46.7% for the 20 ton and 60 ton per day plants.

Impact of Control

Tables 3-77 through 3-79 show the estimated capital outly and operating costs for three current process approaches to dust and fume abatement in the opal glass industry. Because of emissions control, ΔROI is estimated between -2% and -3%.

Table 3-75. Soluble Fluoride Emissions From Opal Glass Production

	1968	2000
CaF_2 utilized in Opal Glass Production (10^3 tons/year)	34.5	57.2
Soluble Fluoride Evolution Factor (lb F/ton CaF_2 fed)	193	193
Soluble Fluoride Emission Factor with Current Control (lb F/ton CaF_2 fed)	193	193
Soluble Fluoride Emission Factor with 99% Control (lb F/ton CaF_2 fed)	-	1.93
Soluble Fluoride Evolution (10^3 tons F/year)	3.32	5.51
Soluble Fluoride Emission with Current Control (10^3 tons F/year)	3.32	5.51
Soluble Fluoride Emission with 99% Control (10^3 tons F/year)	-	0.055

Table 3-76. Estimated Economics of Opal Glass Production (Pollution Control Cost Excluded)

	PLANT CAPACITY	
	20 Tons/Day	60 Tons/Day
TOTAL CAPITAL INVESTMENT(1)	3.2 $MM	5.8 $MM
PRODUCTION COSTS		
DIRECT COSTS		
GLASS SAND (.8 Tons/Net Ton @ 12.75 $/Ton)	10.20 $/Net Ton	10.20 $/Net Ton
SODA ASH (.15 Tons/Net Ton @ 34.00 $/Ton)	5.10	5.10
FLUORSPAR (.16 Tons/Net Ton @ 65.00 $/Ton)	10.40	10.40
BORAX (.01 Tons/Net Ton @ 50.25 $/Ton)	.50	.50
FELDSPAR (.25 Tons/Net Ton @ 20.00 $/Ton)	5.00	5.00
LIMESTONE (.12 Tons/Net Ton @ 4.00 $/Ton)	.48	.48
NATURAL GAS (4.6 MM BTU/Ton X .40 $/MM BTU)	1.84	1.84
LABOR (7 Positions @ 4.00 $/hr)	33.60	11.20
FURNACE REPAIRS (1.2%)	5.82	3.52
FRINGE BENEFITS AND SUPERVISION	33.60	11.20
GENERAL MAINTENANCE AND SUPPLIES (1.25%)	6.08	3.67
TOTAL DIRECT COSTS	112.62	63.11
INDIRECT COSTS		
DEPRECIATION(@ 10%)	48.48	29.29
INTEREST (AT 7%, 20% DEBT)	6.74	4.10
LOCAL TAXES AND INSURANCE (@ 3%)	14.54	8.79
PLANT AND LABOR OVERHEAD	40.32	13.44
TOTAL INDIRECT COSTS	110.13	55.62
TOTAL AVERAGE COST(2) ($/Net Ton)	222.75	118.73
GENERAL AND SALES EXPENSES($/Ton)	4.46 $/Net Ton	2.37 $/Net Ton
F.O.B. COST ($/Net Ton)	227.21 $/Net Ton	121.10 $/Net Ton
AVERAGE PRODUCT REVENUE ($/Ton)	340.00 $/Ton	340.00 $/Net Ton
AVERAGE PROFIT AFTER TAXES (@ 50%)	56.40 $/Ton	109.45 $/Ton
CASH FLOW ($MM/YR)	0.69 $MM/YR	2.75 $MM/YR
RETURN ON INVESTMENT (%)	14.5%	46.7%

(1) Small tank furnace facility

(2) Transporation charges alter costs substantially

Table 3-77. Opal Glass Production - Estimated Economics of Control Process A
Basis - 60 Tons Per Day of Opal Glass Production

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1.	COOLING DUCT, $t_{in} = 1500°F$, $t_{out} = 400°F$, carbon steel, 22,500 cfm, 500 ft^2 surface area, air cooled, 2 in. W.G. pressure drop	3	4383	1.67		5
2.	WET CYCLONE, 100 gal/min, 22,500 cfm, neoprene lined steel, 2 in. W.G. pressure drop	50	4387 4383	1.55		78
	Capital Subtotal					83.
	Indirects (@ 15%)					12.
	Contingency (@ 20%)					17.
	Total Capital (as of January 1971)					112.

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.05	0.10		0.15
2	0.05	0.13		0.18
Subtotal				0.33
Water(21) (100 gpm, 90% recycle)				0.02
Disposal(22)				–
Total Operating Cost				0.35

Total Operating Cost ($/hr)	0.35
Taxes and Insurance (2%, 330 days)	0.28
Capital (7.1%,330 working days)	1.00
Pollution Control Cost ($/hr)	1.63
Pollution Control Cost ($/ton)	0.65

All control economics foot notes are located in Section 3.1.1, pages 3-10 and 3-11.

Table 3-78. Opal Glass Production - Estimated Economics of Control Process B Basis - 60 Tons Per Day of Opal Glass Production

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	COOLING DUCT, t_{in} = 1500°F, t_{out} = 400°F, carbon steel, 22,500 cfm, 500 ft^2 surface area, air cooled, 2 in. W.G. pressure drop	3	4383	1.67		5
2	BAGHOUSE, 22,500 cfm, 2.5 in. W.G. pressure drop, 0.3 lbs solid loading per hour, fabric	20	4383	4.13		83
				Capital Subtotal		88
				Indirects (@ 15%)		13
				Contingency (@ 20%)		18
				Total Capital (as of January 1971)		119

All control economics footnotes are located in Section 3.1.1, page 3-10 and 3-11.

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	.05	0.10		0.15
2	.06	1.26		1.32
Subtotal				1.47
Water[21]				–
Disposal[22]				–
Total Operating Cost				1.47

Total Operating Cost ($/hr)	1.47
Taxes and Insurance (2%, 330 days)	0.30
Capital (7.1%, 330 working days)	1.07
Pollution Control Cost ($/hr)	2.84
Pollution Control Cost ($/ton)	1.14

Table 3-79. Opal Glass Production - Estimated Economics of Control Process C
Basis - 60 Tons Per Day of Opal Glass Production

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	BAGHOUSE, 7500 cfm, 2 lb solid loading per hour, fabric	10.	4383	4.00		40.
					Capital Subtotal	40
					Indirects (@ 15%)	6
					Contingency (@ 20%)	8
					Total Capital (as of January 1971)	54

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.01	1.26		1.27
Subtotal				1.27
Water(21)				–
Disposal(22)				–
Total Operating Cost				1.27

Total Operating Cost ($/hr)	1.27
Taxes and Insurance (2%, 330 days)	0.14
Capital (7.1%, 330 working days)	0.48
Pollution Control Cost ($/hr)	1.89
Pollution Control Cost ($/ton)	0.76

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3.11

3.7 FRIT SMELTING

3.7.1 General

Ceramic coatings are applied to metal, glass, and pottery as protective and decorative coatings. These coatings are applied as mixtures of glassy particles and clay in a water suspension called slip. The glassy particulate, or frit, is produced by melting refractories and flux materials in a furnace followed by quenching and grinding to produce a finely ground, fusable material. The primary elements of frit are refractories and fluxes with minor amounts of colors, opacifiers, and other additives. The fluxes include soda ash, borax, cryolite and fluorspar. Opacifiers of the devitrification type include cryolite and fluorspar; the insoluble opacifiers do not.

3.7.2 Industry Description

The production of enamel glass ("frit") is generally a batch process. After the raw material charge is mixed, the batch is fed to a large hearth smelter and held at temperatures which range to 2700°F until uniformly melted. The melt is poured into a quenching tank of cold water and shatters into the friable particles which constitute the frit. A typical integrated enamel-frit-smelter, sheet-steel-enameling plant is shown in Figure 3-45.

3.7.3 Production Trends

No information is available on the total production of enamel frit. This is due to the fact that a major amount of frit is consumed by cast-iron plumbing fixture manufacturers. These manufacturers do not belong to a representative organization and details on their individual production levels of frit are not available to the public. For this reason, predictions of future production are based on the amount of fluorspar consumed in the manufacture of enamel frit. Predictions of the year 2000 were made on a per-capita consumption basis.

The amount of fluorspar used in frit production will increase from the level of 7800 tons in 1968 to 11,800 tons in 2000 (assuming a per-capita consumption of 0.07 pound). These data are presented in Table 3-80.

3.7.4 Fluoride Control Techniques

Smelting of the frit volatilizes gaseous and particulate fluorides and other very fine particulate matter. Emphasis has been on removal of the

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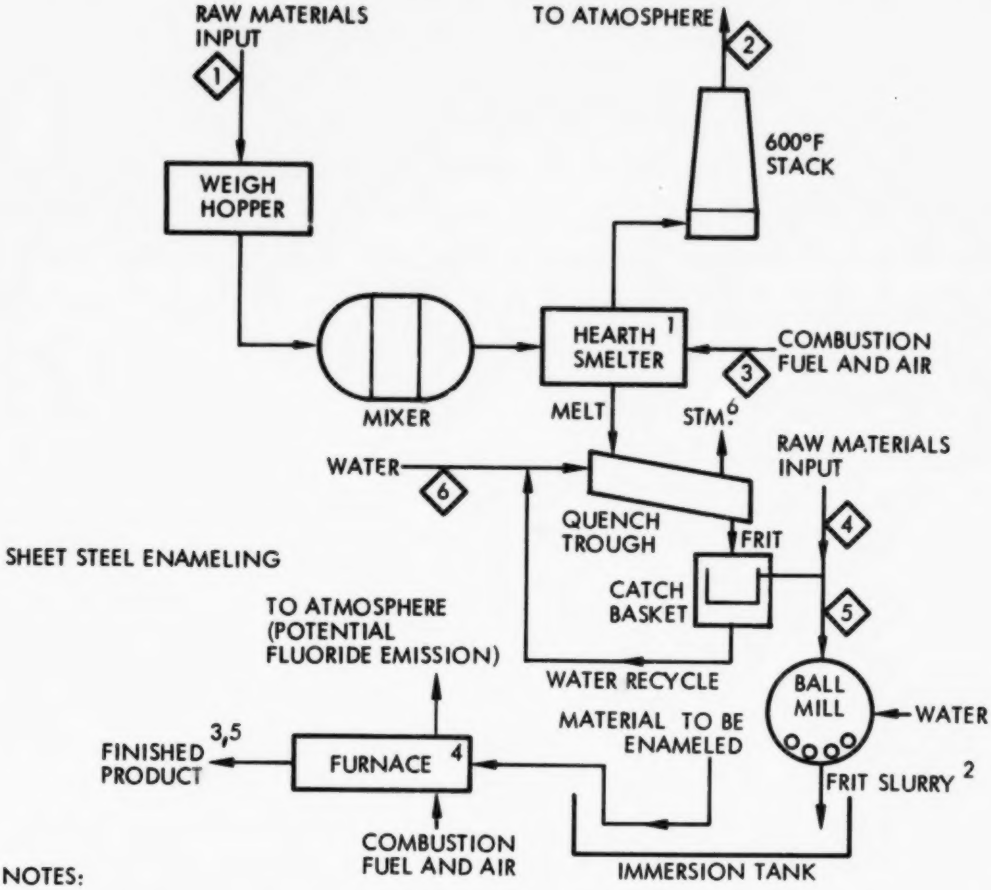

RAW MATERIALS INPUT
1
WEIGH HOPPER
MIXER
TO ATMOSPHERE
2
600°F STACK
HEARTH SMELTER 1
COMBUSTION FUEL AND AIR
3
MELT
STM.6
WATER
6
QUENCH TROUGH
FRIT
RAW MATERIALS INPUT
4
CATCH BASKET
5
WATER RECYCLE
BALL MILL
WATER
TO ATMOSPHERE (POTENTIAL FLUORIDE EMISSION)
MATERIAL TO BE ENAMELED
FINISHED PRODUCT 3,5
FURNACE 4
FRIT SLURRY 2
COMBUSTION FUEL AND AIR
IMMERSION TANK

SHEET STEEL ENAMELING

NOTES:

1. SMELTER OPERATES AT ~ 2700°F SMELTER SIZE ~ 30 LB. OF BATCH PER SQ. FOOT HEARTH.
2. PARTICLE SIZE OF SOLIDS IN THE FRIT SLURRY ARE:
   GROUND COAT (1ST COAT) = 95% THRU 200 MESH
   COVER COAT (2ND COAT) = 98% THRU 325 MESH
3. SHEET STEEL COATINGS USUALLY 5 TO 8 MILS THICK.
4. FIRING TEMPERATURE = 1500° F FOR 5 MIN.
5. MATERIALS BEING ENAMELED MUST BE RECYCLED THROUGH A SECOND COVER COAT AFTER THE INITIAL GROUND COATING.
6. THE EFFLUENT STEAM FROM THE QUENCH TROUGH MAY CONTAIN FLUORIDE COMPOUNDS, LITERATURE SEARCH REVEALED NO DATA.

A

BASI

Mate
HF
NaF
CaF_2
Total Fluo
Total as
Feldspar
Borax
SiO_2
Na_2CO_3
$NaNO_2$
N_2
O_2
CO_2
H_2O
Air (50% R
Natural Ga
CoO
MnO
NiO
Frit
Approximat Stream

*Gaseous effl

(A) Plus mak
(B) Referenc
(C) Referenc
(D) Referenc

Soluble fluor

BASIS - 1000 LBS/HR FEED (STREAMS 1 & 4), SHEET STEEL ENAMELING
PROCESS STREAMS - LBS/HR

Material	Stream Numbers					
	1	2*	3	4	5	6
HF		0.74(g)(Est.)				
NaF		1.55(s)(Est.)				
CaF_2	13 (s)$^{(B,C)}$				10 (s)$^{(C)}$	
Total Fluorides	13	2.3			10	
Total as F	6.3	1.4$^{(D)}$			4.9	
Feldspar	600					
Borax	300					
SiO_2	40					
Na_2CO_3	25	2				
$NaNO_2$	10					
N_2		2700 (g)				
O_2		320 (g)				
CO_2		380 (g)				
H_2O		330 (g)			100	100
Air (50% R.H.)			3500			
Natural Gas			130			
CoO				1		
MnO				4		
NiO				1		
Frit					890	
Approximate Total Stream	990	3700	3600	6	1000	100$^{(A)}$

*Gaseous effluent stream

(A) Plus make-up H_2O for steam loss
(B) Reference 4251
(C) Reference 4257
(D) Reference 4258

Soluble fluoride evolution factor = 3.15 lb F/ton dry frit (215 lb F/ton CaF_2 fed)

Figure 3-45. Enamel Fritting — Uncontrolled Process Model

B

particulate material, and the most frequently used devices are baghouses and venturi scrubbers.(5156) The venturi scrubber approach will remove gaseous fluorides. Although central processes are currently applied to the smelter effluent, it may become necessary to control the quench trough and baking furnace effluents also. Mass balances and process flow diagrams are presented in Figure 3-46 for two currently employed control processes.

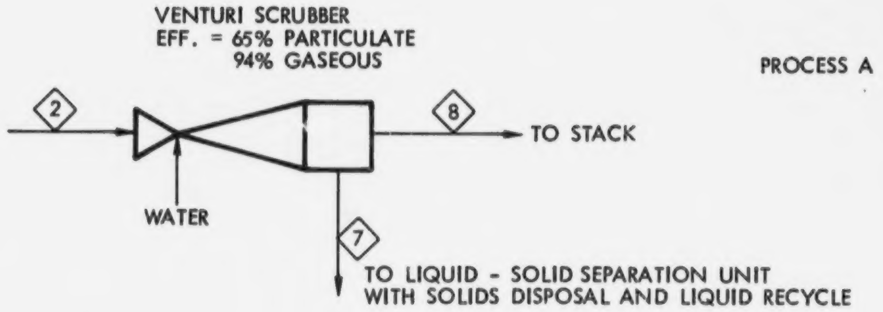
Table 3-80. Enamel Frit Production

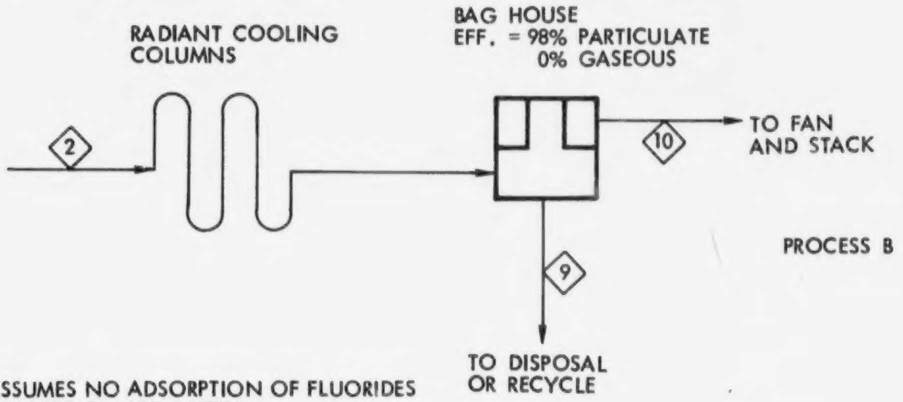
	1967	1968	Estimated(B) to year 2000
Fluorspar used in Frit Production (tons)	4900(4278)	7800(4278)	11,800
U.S. Population (million)	199.1	202.3	336.2(A)
Per-Capita Consumption of Fluorspar used in Frit (pounds)	0.05	0.08	0.07

3.7.5 Fluoride Emissions

Soluble fluoride emissions from the enamel frit industry are estimated at 700 tons in 1968, and are forecast at 1060 tons in 2000, assuming continuation of the use of venturi and wet scrubber control at the current level. It is estimated that only 20% of the operational facilities currently utilize wet scrubbers. If wet scrubber devices are applied throughout the industry and provide abatement at the 99% efficiency level, the soluble fluoride tonnage emitted by the frit industry would drop to about 13 tons in 2000. Table 3-81 presents a summary of these data.

Emission of soluble fluorides from the hearth smelter used for frit production, on the basis of the proprietary thermochemical analyses program, follows a like mechanism to that involved in evolution and emission of soluble fluorides from opal glass furnaces. At the high temperatures present in the hearth, the volatilized fluorides react with water vapor so that at equilibrium, roughly equal molal concentrations of gaseous HF and NaF are formed. When the smelter gas passes into the stack and cools off, the NaF forms a particulate dispersoid fume.


VENTURI SCRUBBER
EFF. = 65% PARTICULATE
94% GASEOUS
PROCESS A
2
8
TO STACK
WATER
7
TO LIQUID - SOLID SEPARATION UNIT
WITH SOLIDS DISPOSAL AND LIQUID RECYCLE


RADIANT COOLING
COLUMNS
BAG HOUSE
EFF. = 98% PARTICULATE
0% GASEOUS
2
10
TO FAN
AND STACK
PROCESS B
9
TO DISPOSAL
OR RECYCLE

NOTE: ASSUMES NO ADSORPTION OF FLUORIDES ON PARTICULATE MATTER.

Material	
HF	0
NaF	1.
Total Fluorides	2.
Total as F	1-
Na_2CO_3	2
N_2	2700
O_2	320
CO_2	380
H_2O	330
Approx. Total Stream	3700

*Gaseous Effluent Stream

(A) Plus scrubbing water and
(B) Utilization of wet control
(C) Reference 5156
(D) Control Processes estimate
remaining 80% uncontrolled.

Source
Smelter Emission
Assumed Fugitive
Total Emission

Overall soluble f

A

BASIS - 1000 LBS/HR FEED, SHEET STEEL ENAMELING PROCESS STREAMS - LBS/HR

	Stream Number				
al	2	7	8*	9	10*
	0.74(g)	0.70 (1)	$0.04(g)^{(C)}$		0.74(g)
	1.55(s)	1.01 (s)	$0.54(s)^{(C)}$	1.52(s)	0.03(s)
orides	2.3	1.71	0.58	1.52	0.77
F	1.4	1.12	0.28	0.69	0.71
	2(s)	$1.3(s)^{(C)}$	$0.7(s)^{(C)}$	$1.96(s)^{(C)}$	$0.04(s)^{(C)}$
	2700(g)		2700(g)	2	2700(g)
	320(g)		329(g)		320(g)
	380(g)		380(g)		380(g)
	330(g)	230(1)	100(g)(Est.)		330(g)
tal	3700	$230^{(A)}$	3500	2	3700

ffluent Stream

scrubbing water and recycled soluble fluorides.
zation of wet control processes
ence 5156
ol Processes estimated to be utilized by 20% of the industry;
ning 80% uncontrolled.

Source	Soluble Fluoride Emission Factor - lb F/ton dry Frit Process A	Process B
Smelter Emission	0.63	1.60
Assumed Fugitive Emission	0	0
Total Emission	0.63	1.60

B

Overall soluble fluoride emission factor = 2.64 lb F/ton dry frit (180 lb F/ton CaF_2 fed)$^{(D)}$

Figure 3-46. Enamel Fritting — Controlled Process Model

Table 3-81. Soluble Fluoride Emissions from Enamel Frit Production

	1968	2000
CaF_2 utilized in Enamel Frit Production (10^3 tons/year)	7.8	11.8
Soluble Fluoride Evolution Factor (lb F/ton CaF_2 fed)	215	215
Soluble Fluoride Emission Factor with Current Control (lb F/ton CaF_2 fed)	180	180
Soluble Fluoride Emission Factor with 99% Control (lb F/ton CaF_2 fed)	-	2.15
Soluble Fluoride Evolved (10^3 tons F/year)	0.84	1.27
Soluble Fluoride Emission with Current Control (10^3 tons/year)	0.70	1.06
Soluble Fluoride Emission with 99% Control (10^3 tons/year)	-	0.013

3.7.6 Economic Analysis

Basic Process. The economics of a characteristic frit production plant are summarized in Table 3-82. While there is a moderate volume of "merchant" frit production for sale, a considerable portion of the frit produced is for captive consumption. Return on investment without fluoride control processes, is estimated at 18.8% (Table 3-82).

Impact of Control. Tables 3-83 and 3-84 present economic analyses of control processes currently employed for abatement of fumes from frit manufacture. ΔROI because of emissions control is estimated as 12%, equivalent to a reduction in ROI to 16.5%, due to the added costs of pollution control.

Table 3-82. Estimated Economics of Enamel Frit Production (Pollution Control Cost Excluded)

Basis - 890 lb/hr Frit Production

Total Capital Investment	1.9	$MM
Production Costs		
Direct Costs		
Fluorspar (0.015 Tons/Net Ton at $65.00/Ton)	.98	$/Net Ton
Feldspar (0.67 Tons/Net Ton at $20.00/Ton)	13.40	
Borax (0.34 Tons/Net Ton at $50.25/Ton)	17.09	
Silica (0.045 Tons/Net Ton at $12.75/Ton)	.57	
Soda Ash (0.028 Tons/Net Ton at $34.00/Ton)	.95	
Soda Niter (0.011 Tons/Net Ton at $213./Ton)	2.34	
Cobalt Oxide (0.0011 Tons/Net Ton at $4400./Ton)	4.84	
Manganese Oxide (0.0045 Tons/Net Ton at $440./Ton)	1.98	
Nickel Oxide (0.0011 Tons/Net Ton at $2700./Ton)	2.97	
Natural Gas (5300 SCF/Ton at $.40/1000 SCF)	2.12	
Water (190 Gal/Ton at $.20/1000 Gal)	.04	
Labor (Four Positions at 4.00 $/hr)	35.96	
Smelter Repairs (1.2%)	6.47	
Fringe Benefits and Supervision	35.96	
General Maintenance and Supplies (1.25%)	6.74	
Total Direct Costs	132.41	
Indirect Costs		
Depreciation (at 7.1%)	38.28	
Interest (at 7%, 20% Debt)	3.36	
Local Taxes and Insurance (at 3%)	16.17	
Plant and Labor Overhead	43.15	
Total Indirect Costs	100.96	
Total Average Costs ($/Net Ton)	233.37	$/Nct ton
General and Sales Expenses ($/Net Ton)	4.67	$/Net ton
F.O.B. Cost ($/Net Ton)	238.04	$/Net ton
Average Product Revenue ($/Net Ton)	400.00	$/Net ton
Average Profit After Taxes (at 50%)	80.98	$/Net ton
Cash Flow ($MM/yr)	0.42	$MM/yr
Return on Investment (%)	18.8%	

Table 3-83. Enamel Fritting - Estimated Economics of Control Process A Basis - 10 Tons of Frit Produced Per Day

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	VENTURI SCRUBBER, t_{in} = 600°F, 0.04 lbs solid/min loading, monel clad, 2300 cfm, 31.5 in W.G. pressure drop	22	4383 4390 4391	1.63		36
					Capital Subtotal	36
					Indirects (@ 15%)	5
					Contingency (@ 20%)	7
					Total Capital (as of January 1971)	48

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.9	0.13		0.22
Subtotal				0.22
Water$^{(21)}$ (20 gpm)				0.01
Disposal$^{(22)}$				–
Total Operating Cost				0.23

Total Operating Cost ($/hr)	0.23
Taxes and Insurance (2%, 330 days)	0.12
Capital (7.1%, 330 working days)	0.34
Pollution Control Cost ($/ hr)	0.69
Pollution Control Cost ($/ton)	1.66

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Table 3-84. Enamel Fritting - Estimated Economics of Control Process B Basis - 10 Tons of Frit Produced Per Day

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	RADIANT COOLING COLUMNS, 1300 ft^2, 2300 cfm, 2 in W.G. pressure drop, carbon steel t_{in}=300°F, t_{out}=150°F	10	4383	1.80		18
2	BAGHOUSE, fabric filter, 2300 cfm, 2.5 in W.G. pressure drop, 1.2 horsepower	20	4383 4387	4.13		83
	Capital Subtotal					101
	Indirects (@ 15%)					15
	Contingency (@ 20%)					20
	Total Capital (as of January 1971)					136

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	–	0.10		0.10
2	0.01	1.26		1.27
Subtotal				1.37
Water(21)				–
Disposal(22)				–
Total Operating Cost				1.37

Total Operating Cost ($/hr)	1.37
Taxes and Insurance (2%,330 days)	0.34
Capital (7.1%, 330 working days)	1.22
Pollution Control Cost ($/ hr)	2.93
Pollution Control Cost ($/ton)	7.03

3.8 HEAVY CLAY PRODUCTS

3.8.1 General

Heavy clay products include the structural elements produced by firing shapes fabricated from common clay with or without glazing, and the refractories and pottery produced by firing shapes fabricated from specialty clays and additives. The structural heavy clay products--brick, pipe, and tile--use over 20 million tons of clay per year. This raw material is reported to contain about 500 parts per million of combined fluorine.(889,4297) The process temperatures (2000-3000°F) required to produce the fired clay products are sufficient to volatilize much of the fluoride content of the feed.

3.8.2 Industry Description

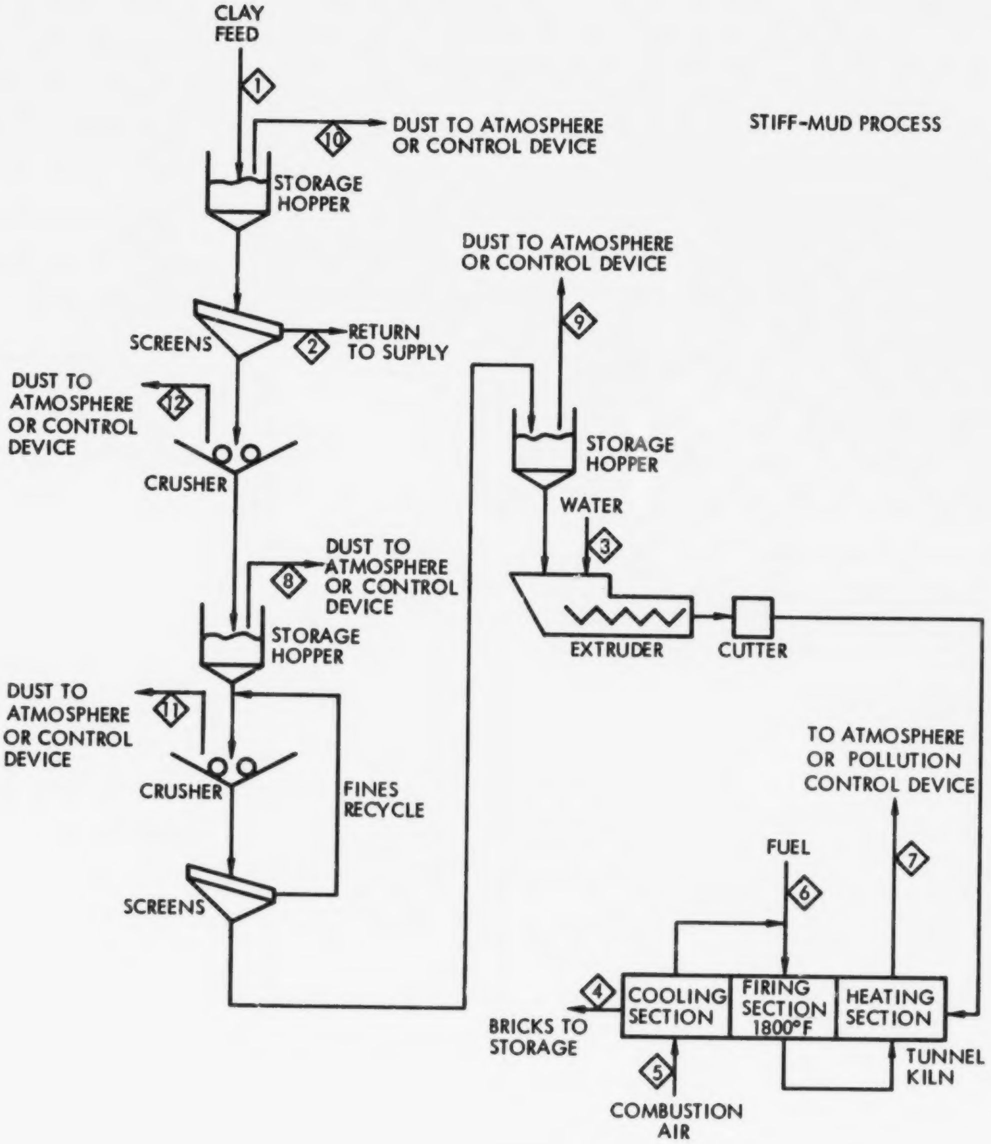
Figure 3-47 presents a flow diagram and mass balance for a typical stiff-mud continuous production brick plant. Soluble fluoride evolution occurs only in the high temperature portions of the tunnel kiln. All of the evolved fluorides are converted to gaseous HF as the result of the high temperature reaction with water vapor.

3.8.3 Production Trends

The use of clay for the production of heavy clay products (mainly brick and tile) has remained relatively constant over the last 15 years. This trend is not expected to change for at least the next 10 years and for purposes of these projections is expected to be unchanged through the year 2000. This would keep the tonnage of clay used for heavy product production at about 23 million tons annually, (4291) as shown in Table 3-85.

Table 3-85. Heavy Clay Product Projections

	1954	1959	1963	1968	Estimated to Year 2000
Clay Usage(4280) (million tons)	23.4	23.3	22.6	23.7	23.5


CLAY FEED
1
10
DUST TO ATMOSPHERE OR CONTROL DEVICE
STORAGE HOPPER
SCREENS
2
RETURN TO SUPPLY
DUST TO ATMOSPHERE OR CONTROL DEVICE
12
CRUSHER
DUST TO ATMOSPHERE OR CONTROL DEVICE
8
STORAGE HOPPER
DUST TO ATMOSPHERE OR CONTROL DEVICE
11
CRUSHER
FINES RECYCLE
SCREENS
DUST TO ATMOSPHERE OR CONTROL DEVICE
9
STORAGE HOPPER
WATER
3
EXTRUDER
CUTTER
TO ATMOSPHERE OR POLLUTION CONTROL DEVICE
FUEL
6
7
4
BRICKS TO STORAGE
COOLING SECTION
FIRING SECTION 1800°F
HEATING SECTION
TUNNEL KILN
5
COMBUSTION AIR

STIFF-MUD PROCESS

Material	
HF	
CaF_2 (Equiv.)	5.0(s
Total Fluorides	5.0
Total as F	2.5
Clay	4,890
H_2O	
Natural Gas	
Air(50% R.H.)	
N_2	
O_2	
CO_2	
Fired Clay Brick	
Approx. Total Stream	4,900

F Evolution Factor = 0.87

*Gaseous Effluent Stream
Soluble Fluoride evoluti
(A) Reference 4297
(B) Reference 889
(C) Reference 4244
(D) Reference 4261

A

BASIS: 50 Tons per day Brick Production
PROCESS STREAMS - LB/HR

Material	Stream Number								
	1	2	3	4	5	6	7*	8*, 9*, 10*	11*, 12*
F							1.79(g)		
aF$_2$ (Equiv.)	5.0(s)$^{(A,B)}$	0.5(s)		0.8(s)$^{(B,D)}$				0.07(s)$^{(D)}$	0.16(s)$^{(D)}$
otal Fluorides	5.0	0.5		0.8			1.79	0.07	0.16
otal as F	2.5	.25		0.4			1.7$^{(B,D)}$	0.035	0.08
lay	4,890	490(Est)						70(s)$^{(D)}$	160(s)$^{(D)}$
$_2$0			500$^{(C,D)}$				1,900(g)		
atural Gas						750			
ir(50% R.H.)					14,000				
$_2$							10,800(g)		
$_2$							650(g)		
$_2$							1,850(g)		
ired Clay rick				4,170					
pprox. Total tream	4,900	490	500	4,170	14,000	750	15,200	70	160

volution Factor = 0.87 lb F/Ton Brick produced

seous Effluent Stream
uble Fluoride evolution factor = 0.81 lb F/ton Product
Reference 4297
Reference 889
Reference 4244
Reference 4261

B

Figure 3-47. Structural Clay Production Uncontrolled Process Model

3.8.4 Fluoride Emission Control Techniques

Figure 3-48 presents process flow diagrams and mass balances for two control processes currently employed in conjunction with structural clay production. Note should be taken that Process B, involving a spray scrubber, is estimated to be used in less than 1 percent of the heavy clay plants.

3.8.5 Fluoride Emissions

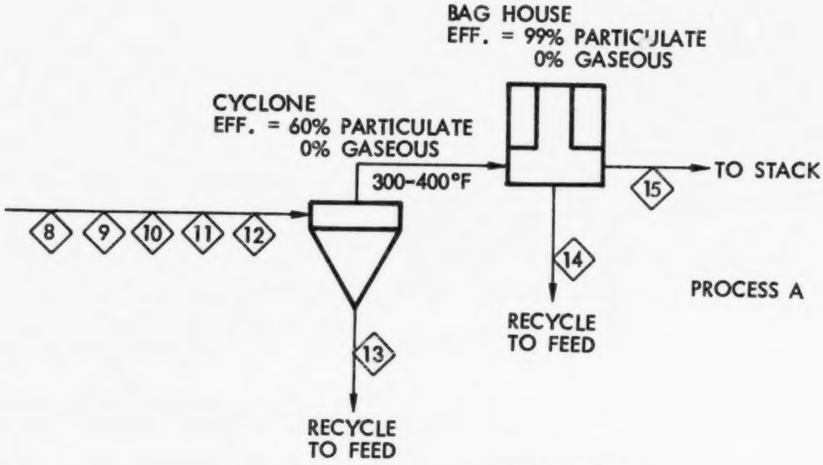
No definitive data exist in the open literature covering the quantities and types of fluorides emitted by the heavy clay industry. Evolution is reported as ranging from 30% to 95% of the feed fluoride content.(889)

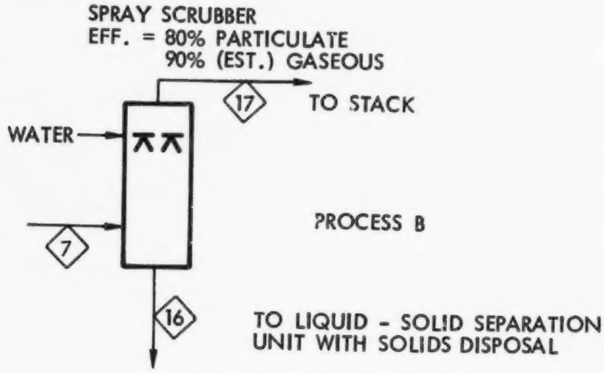
Because of the absence of definitive data in the literature, manufacturing processes for bricks were examined using a proprietary thermochemical analyses program to determine the equilibrium distribution of fluorides in the process outlet streams. If the condensed phases (solid and liquid clay) are in complete chemical equilibrium with the gas phase, all feed fluorine is found as HF in the exhaust gases, with no fluorine remaining as condensed material. Table 3-86 summarizes the input charge composition, the temperature at which the analysis was run, and the resulting concentrations of HF produced in the effluent gas. At the higher temperatures of the actual process, equilibria favor HF even more markedly.

For this study, it was assumed that the feed clay contained 500 ppm of fluoride;(889,4297) that there was 80% evolution (based on partial attainment of thermochemical equilibrium); and that no abatement devices suitable for collection of soluble fluorides were used. On these bases, soluble fluoride emissions will remain constant at the 1970 level of 9700 tons (as F) annually through 2000 if current control policies (which are essentially no fluoride control) are continued. If control processes with 99% efficiency are applied on an industry wide basis, the heavy clay industry would emit 97 tons of fluoride in 2000. Table 3-87 is a summary of the above data.

3.8.6 Economic Analysis

Basic Process. Table 3-88 presents an analysis of the economics of structural clay production for a typical 50 ton per day brick plant. Return on investment, prior to use of soluble fluoride control processes, is estimated as 11.3%.


BAG HOUSE
EFF. = 99% PARTICULATE
0% GASEOUS
CYCLONE
EFF. = 60% PARTICULATE
0% GASEOUS
300-400°F
TO STACK
15
8
9
10
11
12
14
PROCESS A
RECYCLE
TO FEED
13
RECYCLE
TO FEED


SPRAY SCRUBBER
EFF. = 80% PARTICULATE
90% (EST.) GASEOUS
17
TO STACK
WATER
PROCESS B
7
16
TO LIQUID - SOLID SEPARATION
UNIT WITH SOLIDS DISPOSAL

Material	
	7
HF CaF_2 equiv.	1.79(g)
Total Fluorides	1.79
Total as F	1.7
Clay (dust)	
H_2O	1900(g)
N_2	10800(g)
O_2	650(g)
CO_2	1850(g)
Approx. Total Stream	15200

*Gaseous Effluent Stream

(A) Plus water and soluble fluo

(B) Water soluble fluorides

(C) Plus dilution air

(D) Utilization of soluble fluo

(E) Reference 4261

Sou
Kiln Effluent
Dust Emissions
Assumed Fugitive
Total Soluble Fl

Overall Soluble

A

BASIS - 50 TONS PER DAY BRICK PRODUCTION

PROCESS STREAMS - LB/HR.

	Stream Number						
	7	8, 9, 10, 11, 12	13	14	15*	16	17*
	1.79(g)					1.61$^{(\ell)}$	0.18(g)$^{(E)}$
		0.23(s)	0.14(s)$^{(E)}$	0.089(s)$^{(E)}$	0.001(s)$^{(E)}$		
es	1.79	0.23	0.14	0.089	0.001	1.61	0.18
	1.7	0.12	0.07	0.044	0.0005	1.53$^{(B)}$	0.17
		230(s)	140(s)$^{(E)}$	89(s)$^{(E)}$	1(s)$^{(E)}$		
	1900(g)					1500(1)(Est)	400(g)(est)
	10800(g)						10800(g)
	650(g)						650(g)
	1850(g)						1850(g)
	15200	230$^{(C)}$	140	90	1$^{(C)}$	1500$^{(A)}$	15200

ent Stream

and soluble fluorides

uble fluorides

ion air

n of soluble fluoride controlling processes (Process B) estimated to be less than 1 percent

4261

Source	Soluble Fluoride Emission Factor - lb F/ton Product	
	Process A	Process B
Kiln Effluent	0.081	-
Dust Emissions	-	0
Assumed Fugitive	0	0
Total Soluble Fluoride Emission	0.081	0

Overall Soluble fluoride emission factor = 0.81 lb F/ton Product$^{(D)}$

Figure 3-48. Structural Clay Production — Controlled Process Model

B

Table 3-86. Brick Production Process Charge Composition

	Weight %	Mole %
SiO_2	15.43	7.912
Al_2O_3	3.88	1.173
Fe_2O_3	1.24	0.239
MgO	0.35	0.268
CaO	0.35	0.192
Na_2O	0.20	0.099
K_2O	0.75	0.245
CaF_2	0.015	0.006
H_2O	5.45	9.333
N_2	52.70	58.019
O_2	15.91	15.326
CH_4	3.73	7.186

Fluoride Distribution
at 1700F

Product Compound	Concentration In Gas	% of Total Fluoride Charged
HF	128.3 ppm	100.

Table 3-87. Soluble Fluoride Emissions from Structural Clay Production

	1968	2000
Heavy clay production (10^6 tons/year)	24	24
Soluble Fluoride Evolution Factor (lb F/ton product)	0.81	0.81
Soluble Fluoride Emission Factor with Current Practice (lb F/ton product)	0.81	0.81
Soluble Fluoride Emission Factor with 99% Control (lb F/ton product)	-	0.0081
Soluble Fluoride Evolved (10^3 tons/year)	9.72	9.72
Soluble Fluoride Emissions with Current Practice (10^3 tons/year)	9.72	9.72
Soluble Fluoride Emissions with 99% Control (10^3 tons/year)	-	0.097

Table 3-88. Estimated Economics of Structural Clay Production(A) (Pollution Control Cost Excluded)

	Plant Capacity 50 tons/day
Installed Capital Investment	2.3 $MM
Operating Costs	
Direct Costs	
Clay (1.2 tons/ton product at $2.50/ton)	3.00$/ton
Water (30 gal/ton product at $0.03/1000 gal)	0.01
Natural Gas (6800 scf/ton at $0.35/1000 scf)	2.38
Electric Energy (98 kwh/ton at $0.007/kwh)	0.69
Operating Labor (4.00 $/hr)	3.84
Supervision and Fringe Benefits	3.84
Maintenance and Fringe Benefits (at 5% of Capital/Year)	7.67
Total Direct Costs	21.43
Indirect Costs	
Depreciation (at 4%/yr)	6.14
Interest (at 7%, 20% Debt)	2.15
Insurance and Local Taxes	4.60
Overhead	4.61
Total Indirect Costs	17.50
Total Manufacturing Cost ($/ton)	38.93
General and Sales Expenses ($/ton)	0.78
F.O.B. Cost ($/ton)	39.71
Average Product Revenue ($/ton)	67.45
Profit After Taxes (at 50%)	13.87 $/ton
Cash Flow ($MM/yr)	0.30 $MM/yr
Return on Investment(B)	11.3%

(A) Assuming 300 operating days per year

(B) Assumes 80% equity funding

Impact of Control. Tables 3-89 and 3-90 present analyses of the control systems currently employed in conjunction with heavy clay products. ΔROI due to emission control is estimated as -2 to -4%, decreasing ROI to about 11%.

Table 3-89. Structural Clay Production - Estimated Economics of Control Process A Basis - 50 Tons of Brick Produced Per Day

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	CYCLONE 1500 cfm, carbon steel 400°F, 4.9 in W.G. pressure drop, 2 horsepower requirement	3.0	4387 4390 4392	2.00		6.0
2	BAGHOUSE, 1500 cfm, 2.5 in W.G. pressure drop, fabric filter	4.0	4383	4.13		16.0
	Capital Subtotal					22.0
	Indirects (@ 15%)					3.3
	Contingency (@ 20%)					4.4
	Total Capital (as of January 1971)					29.7

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.01	0.13		0.14
2	0.01	1.26		1.27
Subtotal				1.41
Water(21)				–
Disposal(22)				–
Total Operating Cost				1.41

Total Operating Cost ($/hr)	1.41
Taxes and Insurance (2%,300 days)	0.08
Capital (6.7%, 300 working days)	0.28
Pollution Control Cost ($/ hr)	1.77
Pollution Control Cost ($/ton)	0.85

Table 3-90. Structural Clay Production - Estimated Economics of Control Process B
Basis - 50 Tons of Brick Produced Per Day

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	SPRAY SCRUBBER, 6000 cfm 4 ft diameter by 8 ft, 2 in W.G. pressure drop, neoprene lined steel 0.03 lbs HF(g)/min, 2.5 horsepower, 130 gal/min	5.4	4387 4391 4383	2.67		14.4
				Capital Subtotal		14.4
				Indirects (@ 15%)		2.2
				Contingency (@ 20%)		2.9
				Total Capital (as of January 1971)		19.5

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.02	0.25		0.27
Subtotal				0.27
Water[(21)] (130 gpm, 90% recycle)				0.02
Disposal[(22)]				-
Total Operating Cost				0.29

Total Operating Cost ($/hr)	0.29
Taxes and Insurance (2%,300 days)	0.05
Capital (6.7%, 300 working days)	0.18
Pollution Control Cost ($/ hr)	0.52
Pollution Control Cost ($/ton)	0.25

3.9 EXPANDED CLAY AGGREGATE

3.9.1 General

Expanded clay aggregate manufacture produces fired, low-density high-crush-strength pellets from clay for use in high strength concrete. The bulk of the production is employed by the construction industry as a light-weight aggregate replacement for gravel in structural concrete.

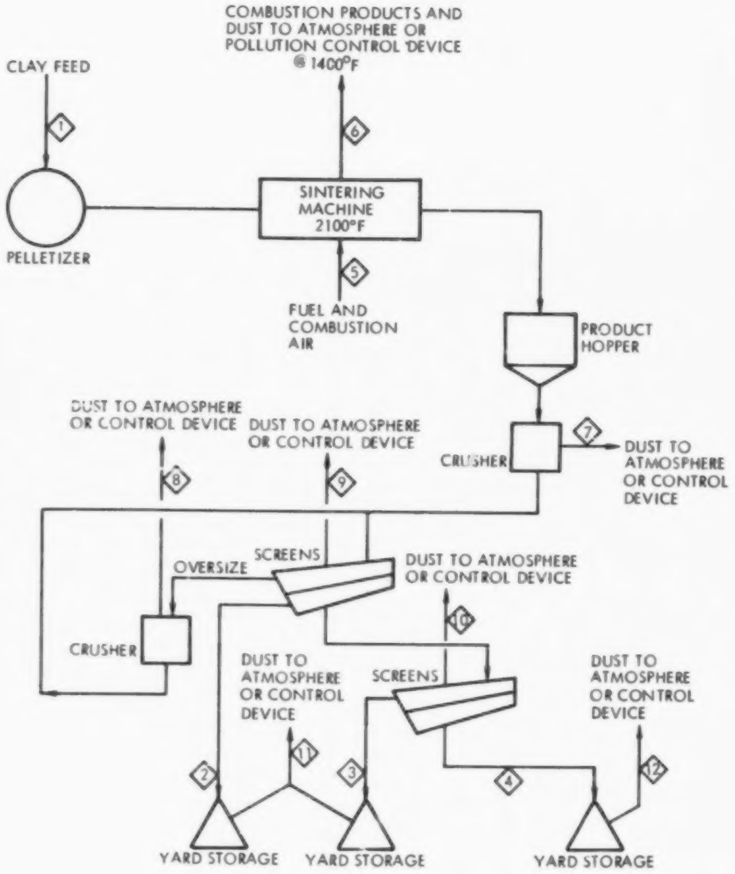
3.9.2 Industry Description

Figure 3-49 presents a flow diagram and mass balance for a 400-ton per day continuous production, expanded clay aggregate plant. (Production is normally rated in cubic yards, with 1 cubic yard roughly equivalent to 1 ton.)

Small pellets (1/4 x 1/2 inch) are formed in the pelletizer from clay material, with added small amounts of oil and water. The pelletized clay is fired in a sintering machine (generally a rotary kiln) to product temperatures ranging between 1850° and 2100°F. The fired clay pebbles are cooled and conveyed to storage after screening. Gaseous HF is evolved in the sintering machine as the result of the high temperature reaction between volatilized CaF_2 and water vapor.

3.9.3 Production Trends

Current (1968) use of expanded clay aggregate is estimated at 9 million tons. Very little information is available on the projected use of this product. The Bureau of Mines reports that the production of clay and shale for lightweight aggregates will probably continue to increase at a rate above that of GNP but not as rapidly as it has during the past 10 years.(4291) For purposes of this projection the GNP is estimated to increase at a rate of 4.3%(4250) annually. The estimated increase in production was assumed to be 5% compounded annually. This would put the usage of clay for expanded clay aggregate at 44 million tons in 2000. As indicated by recent practice, new plants will be larger and more efficient. Table 3-91 presents the past, current and projected production tonnages for expanded clay aggregate.


COMBUSTION PRODUCTS AND DUST TO ATMOSPHERE OR POLLUTION CONTROL DEVICE @ 1400°F
CLAY FEED
1
PELLETIZER
6
SINTERING MACHINE 2100°F
5
FUEL AND COMBUSTION AIR
PRODUCT HOPPER
DUST TO ATMOSPHERE OR CONTROL DEVICE
DUST TO ATMOSPHERE OR CONTROL DEVICE
8
9
7
CRUSHER
DUST TO ATMOSPHERE OR CONTROL DEVICE
OVERSIZE
SCREENS
DUST TO ATMOSPHERE OR CONTROL DEVICE
10
CRUSHER
DUST TO ATMOSPHERE OR CONTROL DEVICE
SCREENS
DUST TO ATMOSPHERE OR CONTROL DEVICE
11
2
3
4
12
YARD STORAGE
YARD STORAGE
YARD STORAGE

BASIS - 400 TONS/DAY OF EXPANDED CLAY AGGREGATE PRODUCED

PROCESS STREAMS - LB/HR.

Materials	Stream Number 1	 2,3,4	 5	 6*	 7*,8*,9*,10*,11*,12*
HF				20.0(g)	
CaF_2 Equiv.	46(s)$^{(A,B,D)}$	6.8(s)$^{(B,C)}$			0.2(s)$^{(C)}$
Total Fluorides	46	6.8		20.0	0.2
Total as F	22.4	3.3		19.0$^{(B,C)}$	0.1
Clay	44,400			200(s)$^{(C)}$	200(s)$^{(C)}$
Natural Gas			2,700(Est)		
Air(50% R. H.)			50,800(Est)		
N_2				39,100(g)	
O_2				2,000(g)	
CO_2				12,700(g)	
H_2O				10,400(g)	
Expanded Clay Aggregate		33,300			
Approx. Total Streams	44,400	33,300	53,500	64,400	200

F Evolution Factor = 1.5 lb F/ton expanded clay product

* Gaseous Effluent Stream

Soluble fluoride evolution factor = 1.14 lb F/ton aggregate

(A) Reference 4297

(B) Reference 889

(C) Reference 4262

(D) Does not include fluorides recycled from emission control devices.

Figure 3-49. Expanded Clay Aggregate — Uncontrolled Process Model

Table 3-91. Expanded Clay Aggregate Projections

	1958	1968	Past 10 Yr Annual Growth Rate(B)	Estimated GNP(4250) Growth Rate to 2000	Estimated(A) Usage in Year 2000
Clay Usage (Million tons)	4.46(4278)	9.28(4278)	7.6%	4.3%	44.2

(A) Growth rate assumed to be 5% annually.

(B) Growth rates compounded annually.

3.9.4 Fluoride Emission Control Techniques

The application of processes capable of controlling soluble fluoride emissions to the production of expanded clay aggregate is estimated as covering less than 1% of the currently used production capacity. Figure 3-50 presents flow diagrams and mass balances for the two currently employed emission control systems; only Process A is capable of abatement of the gaseous HF emitted by the sintering machine (kiln).

3.9.5 Fluoride Emissions

There is the same lack of published information on the fluoride species and quantities emitted in the manufacture of expanded clay aggregate as was noted for the heavy clay products industry. Because of the physicochemical similarity of the two processes, the assumptions and thermochemical models used to estimate heavy clay fluoride emissions were used to estimate soluble fluoride emissions from the expanded clay aggregate industry. Charge composition and theoretical equilibrium evolved gas composition are shown in Table 3-92.

Based on the logic discussed in Section 3.8, soluble fluoride emissions will increase from 5300 tons annually in 1968 to about 25,100 tons annually in 2000, if the current lack of control continues. If high efficiency (99%) control technology is employed, estimated soluble fluoride emissions will drop to 250 tons annually in 2000. These data are summarized in Table 3-93.

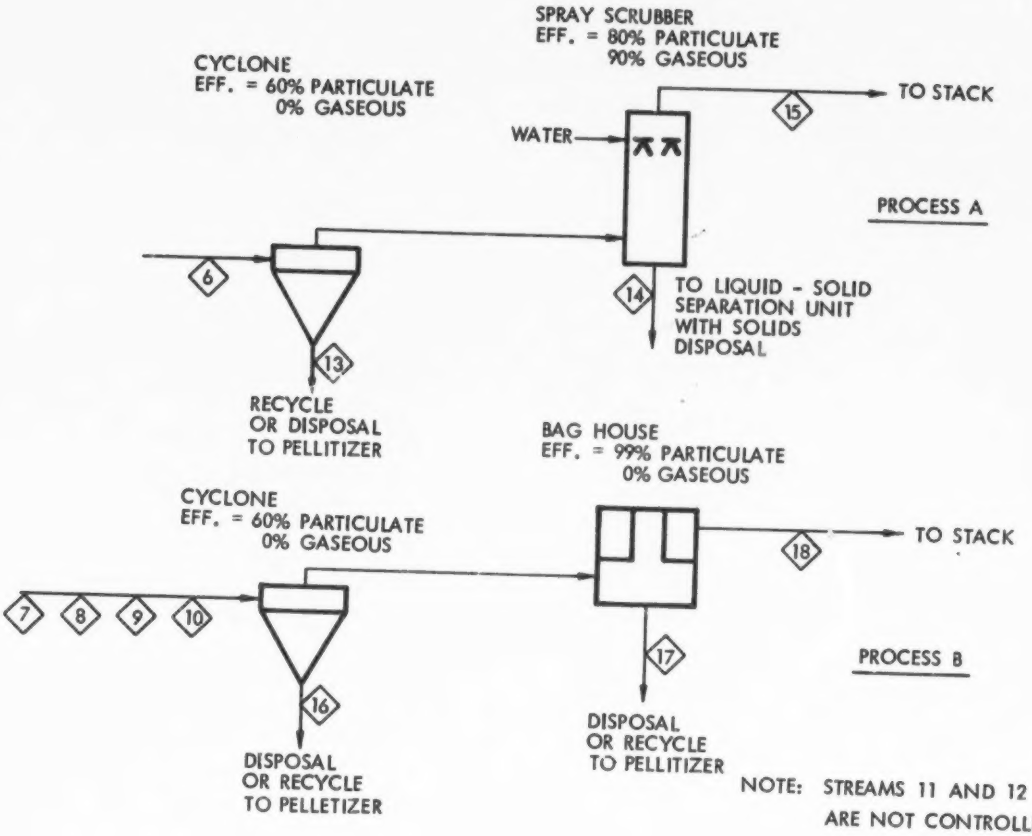
3.9.6 Economic Analysis

Basic Process

Table 3-94 summarizes the economic analysis of expanded clay aggregate production for a 400 ton per day plant. Return on investment, without control processes, is estimated at 31.7%.

Impact of Control

Tables 3-95 and 3-96 summarize the cost of fluoride pollution control, using Processes A and B as presented in Figure 3-50, Controlled Process Model.


SPRAY SCRUBBER
EFF. = 80% PARTICULATE
90% GASEOUS
CYCLONE
EFF. = 60% PARTICULATE
0% GASEOUS
WATER
TO STACK
15
PROCESS A
6
14
TO LIQUID - SOLID SEPARATION UNIT WITH SOLIDS DISPOSAL
13
RECYCLE OR DISPOSAL TO PELLITIZER
BAG HOUSE
EFF. = 99% PARTICULATE
0% GASEOUS
CYCLONE
EFF. = 60% PARTICULATE
0% GASEOUS
TO STACK
18
7
8
9
10
17
PROCESS B
16
DISPOSAL OR RECYCLE TO PELLITIZER
DISPOSAL OR RECYCLE TO PELLETIZER

NOTE: STREAMS 11 AND 12 ARE NOT CONTROLLED.

Material	
HF	
CaF_2 Equiv.	
Total Fluorides	
Total as F	1
Clay (dust)	20
N_2	39
O_2	2
CO_2	12
H_2O	10
Approx. Total Stream	64

*Gaseous Effluent

(A) Plus dilution
(B) Assumes a 50/
(C) Plus scrubber
(D) Utilization o
less than 1 p
(E) Reference 426

So
Sintering Machin
Dust Evolution
Assumed Fugitiv
Total Soluble Fl

Overall Soluble Flu

A

BASIS - 400 TONS/DAY OF EXPANDED CLAY AGGREGATE PRODUCED

PROCESS STREAMS - LB/HR

Material	Stream Number								
	6	7,8,9,10	11*,12*	13	14	15*	16	17	18*
HF	20.0(g)				18.0	2.0(g)$^{(E)}$			
CaF_2 Equiv.		0.1(s)(Est.)	0.1(s)(Est.)				0.06(s)$^{(4(E)}$	0.039(s)$^{(4}$	0.001(s)$^{(E)}$
Total Fluorides	20.0	0.1	0.1		18.0	2.0	0.06	0.039	0.001
Total as F	19.0	0.05	0.05		17.1	1.9	0.03	0.019	0.005
Clay (dust)	200(s)	100(s)(Est.)	100(s) (Est.)	120(s)$^{(E)}$	64(s)$^{(E)}$	16(s)$^{(E)}$	60(s)$^{(E)}$	39(S)$^{(E)}$	1(s)$^{(E)}$
N_2	39100(g)					39100(g)			
O_2	2000(g)					2000(g)			
CO_2	12700(g)					12700(g)			
H_2O	10400(g)				8800(1)	1600(g)(Est)			
Approx. Total Stream	64400	100$^{(A,B)}$	100	120	9000$^{(C)}$	53000	60	40	1

*Gaseous Effluent Stream

(A) Plus dilution air.
(B) Assumes a 50/50 split of the total amounts from streams 7, 8, 9, 10, 11, 12.
(C) Plus scrubber water and recycled soluble fluorides.
(D) Utilization of soluble fluoride controlling processes (Process A) estimated to be less than 1 percent.
(E) Reference 4262.

Source	Soluble Fluoride Emission Factor lb F/ton Aggregate	
	Process A	Process B
Sintering Machine	0.11	-
Dust Evolution	-	0
Assumed Fugitive Emission	0	0
Total Soluble Fluoride Emission	0.11	0

Overall Soluble Fluoride Emission Factor = 1.14 lb F/ton$^{(D)}$ Aggregate.

Figure 3-50. Expanded Clay Products — Controlled Process Model

B

Table 3-92. Expanded Clay Process Charge Composition

	Weight %	Mole %
SiO_2	28.17	16.529
Al_2O_3	7.27	2.514
Fe_2O_3	2.25	0.497
MgO	0.67	0.586
CaO	0.67	0.421
Na_2O	0.41	0.233
K_2O	1.33	0.498
CaF_2	0.03	0.012
H_2O	4.92	9.636
N_2	39.53	49.772
O_2	11.98	13.199
CH_4	2.77	6.104

Fluoride Distribution
at 1900F

Product Compound	Concentration in Gas	% of Total Fluoride Charged
HF	279.9 ppm	100.

Table 3-93. Soluble Fluoride Emissions from Expanded Clay Aggregate Production

	1968	2000
Clay Aggregate Produced (10^6 tons/year)	9.3	44
Soluble Fluoride Evolution Factor (lb F/ton Aggregate)	1.14	1.14
Soluble Fluoride Emission Factor with Current Practice$^{(A)}$ (lb F/ton Aggregate)	1.14	1.14
Soluble Fluoride Emission Factor with 99% Control (lb F/ton Aggregate)	-	0.011
Soluble Fluoride Evolved (10^3 tons F/year)	5.30	25.1
Soluble Fluoride Emissions with Current Practice (10^3 tons F/year)	5.30	25.1
Soluble Fluoride Emissions with 99% Control (10^3 tons F/year)	-	0.25

(A) No fluoride emission control.

Table 3-94. Estimated Economics of Expanded Clay Products[(A)]
(Pollution Control Cost Excluded)

	Plant Capacity 400 tons/day
Installed Capital Investment	0.45 \$MM
Operating Costs	
Direct Costs	
Clay (1.4 tons/ton product at \$2.50)	3.50 \$/ton
Natural Gas (3800 scf/ton at 0.35 \$/1000 scf)	1.35
Electric Energy (62 kwh/ton at 0.007\$/kwh)	0.43
Operating Labor (at 4.00 \$/hr)	0.96
Supervision and Fringe Benefits	0.96
Maintenance and Supplies (at 4% of investment/yr)	0.15
Total Direct Costs	7.35
Indirect Costs	
Depreciation (at 10% per yr)	0.38
Interest (at 7%, 20% Debt)	0.05
Insurance and Local Taxes	0.11
Plant and Labor Overhead	1.15
Total Indirect	1.69
Total Manufacturing Cost	9.04
General and Sales Expenses (\$/ton)	0.18
F.O.B. Cost (\$/ton)	9.17
Average Product Revenue	11.06
Profit After Taxes (taxed at 50%)	0.95 \$/ton
Cash Flow (\$MM/yr)	0.16 \$MM/yr
Return on Investment[(B)]	31.7%

(A) Assumes 300 operating days per year.

(B) Assumes 80% equity funding.

Table 3-95. Expanded Clay - Estimated Economics of Control Process A
Basis - 400 Tons Per Day of Expanded Clay Aggregate Production

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	CYCLONE, 16,000 cfm, 3.33 lbs solid/min, neoprene lined steel, 4.9 in W.G. pressure drop, 16.5 horsepower	15.0	4387 4390 4392	2.07		31.0
2	SPRAY SCRUBBER, 16,000 cfm, 5 ft diameter by 12 ft, neoprene lined steel, 360 gal/min, 2 in W.G. pressure drop, 8 horsepower	20.0	4386 4387 4391	2.40		24.0
3	LIQUID-SOLID SEPARATOR, 360 gal/min, 3.3 lbs/min loading, 22,000 gal capacity, neoprene lined steel	19.0	4398 4392	4.26		81.0
				Capital Subtotal		136.0
				Indirects (@ 15%)		20.0
				Contingency (@20%)		27.0
				Total Capital (as of January 1971)		183.0

All control economics footnotes are located in Section 3.1.1pages3-10 and3-11

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.9	0.13		0.22
2	0.4	0.25		0.29
3	-	0.06		0.06
Subtotal				0.57
Water[21] (360 gpm, 90 % recycle)				0.04
Disposal[22]				-
Total Operating Cost				0.61

Total Operating Cost ($/hr)	0.61
Taxes and Insurance (2%, 300 days)	0.51
Capital (6.7%, 300working days)	1.70
Pollution Control Cost ($/hr)	2.82
Pollution Control Cost ($/ton)	0.17

Table 3-96. Expanded Clay Products - Estimated Economics of Control Process B Basis - 400 Tons Per Day of Expanded Clay Aggregate Production

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	CYCLONE, 5,000 cfm, 4.9 in W.G. pressure drop, carbon steel, 5 horsepower	3.0	4387 4390 4392	3.0		9.0
2	BAGHOUSE, 5,000 cfm, 4.9 in W.G. pressure drop, fabric filter-shaker, 3 horsepower	9.0	4387 4383	4.13		36.0
					Capital Subtotal	45.0
					Indirects (@ 15%)	6.8
					Contingency (@ 20%)	9.0
					Total Capital (as of January 1971)	60.8

All control economics footnotes are located in Section 3.1.1, page 3-10 and 3-11.

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.04	0.13		0.15
2	0.02	1.26		1.28
Subtotal				1.43
Water(21)				–
Disposal(22)				–
Total Operating Cost				1.43

Total Operating Cost ($/hr)	1.43
Taxes and Insurance (2%,300 days)	0.17
Capital (6.7%, 300 working days)	0.57
Pollution Control Cost ($/hr.)	2.17
Pollution Control Cost ($/ton)	0.13

3.10 CEMENT MANUFACTURE

3.10.1 General

Portland cement is manufactured in this country at the rate of almost 100 million tons per year by grinding the clinkers resulting from the calcination of mixtures of clay and limestone in rotary kilns. Blast furnace slag, by product calcium carbonate, gypsum, sand, waste bauxite and iron ore are frequently used in varying quantities, in addition to the clay and limestone. The major raw materials contain calcium fluoride; during the direct-fired kiln calcination process, the calcium fluoride serves as a source material for the evolution of gaseous HF.

3.10.2 Industry Description

Process models covering the wet and dry processes for the manufacture of portland cement are presented in Figures 3-51 and 3-52. The plant sizes selected were 10,000 barrels per day. In both wet and dry processes, current practice charges the materials in the necessary proportions to the closed circuit grinding system used to obtain the physical size and intimate contact required for the chemical conversions which take place in the kiln. The heat required for the chemical conversions is provided by direct-firing the kiln with oil, gas or pulverized coal. The kilns are the major points of fluoride evolution in the cement processes.

3.10.3 Production Trends

The cement industry will continue to expand both in response to population growth and to growing need in highway, industrial and housing construction. Estimates of the future demand for this material are based on long-term per-capita consumption rates and historical market trends. Production has increased at an average annual rate of 3.7% (200 MM bbls in 1949 to 360 MM bbls in 1964) since 1949.(4292)

On a per-capita basis, consumption of portland cement can be expected to rise to almost two barrels per person by 1975. In the past decade the per-capita average has been about 1.8 barrels.(4292) Some increase over the present level is expected because much of the net increase in population in the next 10 years will occur in states where per-capita use of cement is considerably above the national average. Consumption of

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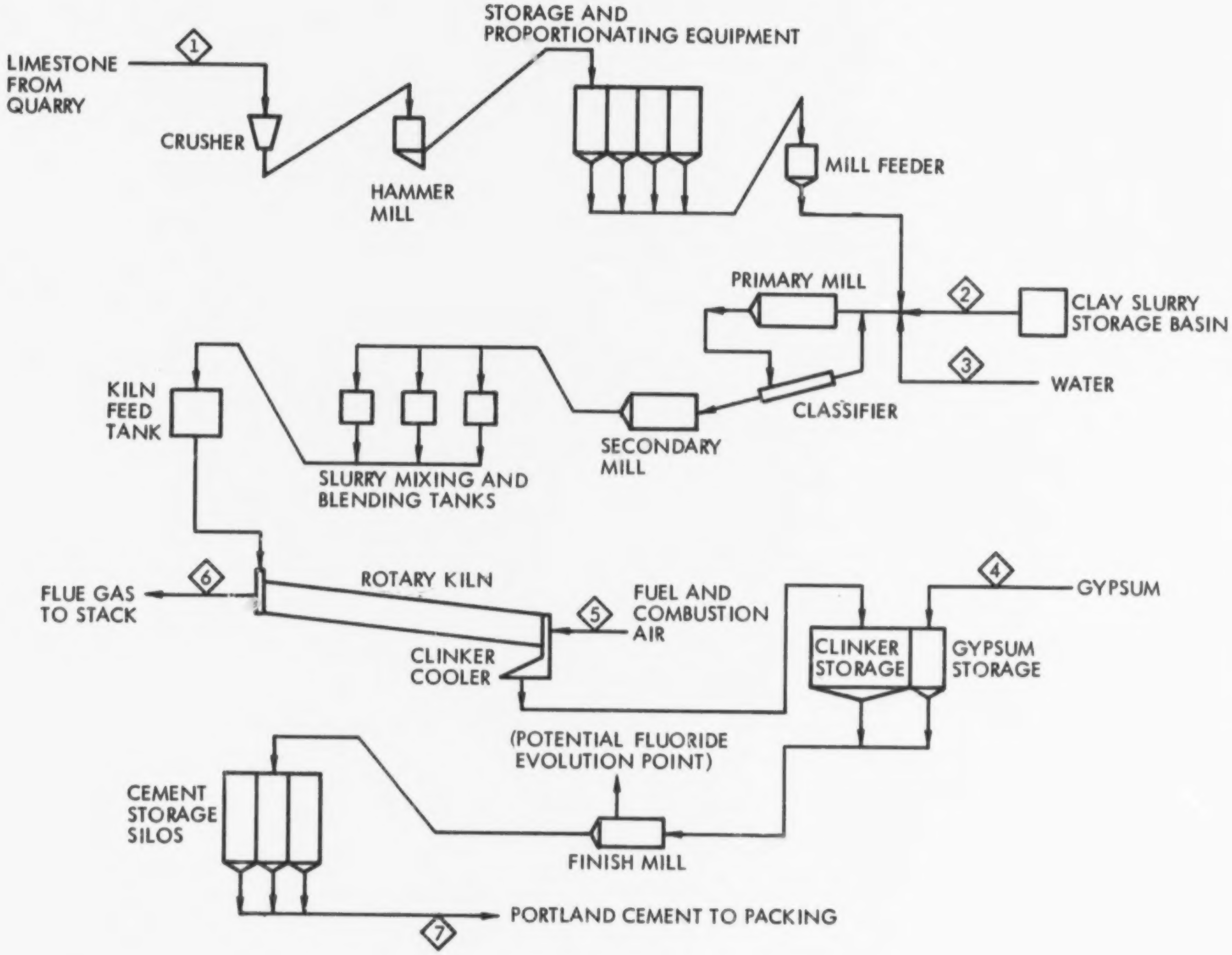
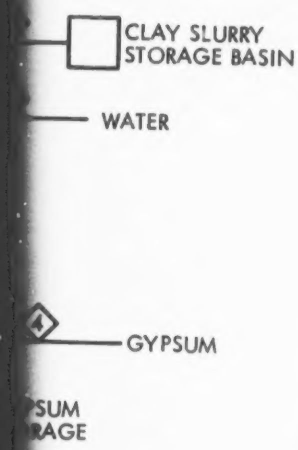

STORAGE AND PROPORTIONATING EQUIPMENT
1
LIMESTONE FROM QUARRY
CRUSHER
HAMMER MILL
MILL FEEDER
PRIMARY MILL
2
CLAY SLURRY STORAGE BASIN
3
WATER
CLASSIFIER
SECONDARY MILL
KILN FEED TANK
SLURRY MIXING AND BLENDING TANKS
ROTARY KILN
6
FLUE GAS TO STACK
5
FUEL AND COMBUSTION AIR
CLINKER COOLER
4
GYPSUM
CLINKER STORAGE
GYPSUM STORAGE
(POTENTIAL FLUORIDE EVOLUTION POINT)
CEMENT STORAGE SILOS
FINISH MILL
7
PORTLAND CEMENT TO PACKING

A



BASIS: WET PROCESS MANUFACTURE OF PORTLAND CEMENT
AT 10,000 BBL PER DAY
PROCESS STREAMS - TONS/DAY

Materials	Stream Numbers						
	1	2	3	4	5	6*	7
HF						$0.008(g)^{(D)}$	
CaF_2 (Equiv.)	3.35(Est)	0.82(Est)				$4.17\ (s)^{(D)}$	
Total Fluoride	3.35	0.82				4.17	
Total as F	1.63(Est)	0.40(Est)				2.03	
Limestone	$2500(s)^{(E)}$						
Shale (Clay)		$620(s)^{(E)}$					
Water			$1600(l)^{(A)}$				
Gypsum				$80(s)^{(E)}$			
Fuel**							
Coal					$530(s)^{(E)}$		
Oil***					$92,000(l)^{(B)}$		
Natural Gas****					$8,800(g)^{(E)}$		
Flue Gas****						$270,000(g)^{(C)}$	
Flue Particulates						$190(s)^{(C)}$	
Portland Cement							*****$^{(B)}$ 1880 (s)
Approx. Total Stream	2500	620	1600	80	-	-	1880

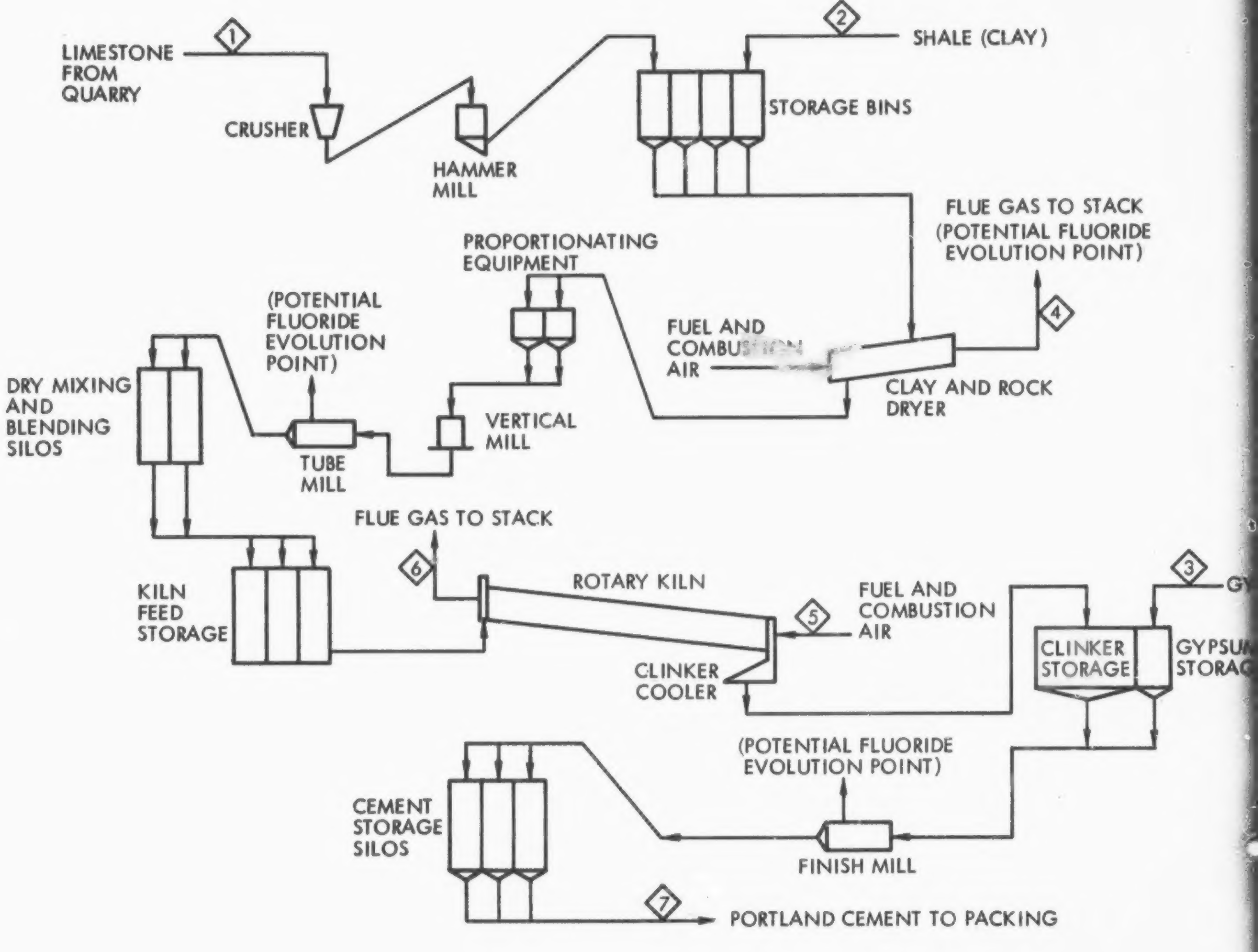
* Gaseous Evolution stream
** Coal, oil and natural gas fuel options are presented
*** Gal per day
**** SCFM (1 atm, 60°F)
***** Equivalent to 10,000 bbl per day

Soluble fluoride evolution factor = 0.008 lb F/ton of cement (16 lb F/10^4 bbl of cement).

(A) Reference 2220
(B) Reference 2027
(C) Reference 4298
(D) Reference 4266
(E) Reference 4244

B

Figure 3-51. Wet Process Portland Cement Production — Uncontrolled Process Model


LIMESTONE FROM QUARRY
1
CRUSHER
HAMMER MILL
2
SHALE (CLAY)
STORAGE BINS
FLUE GAS TO STACK (POTENTIAL FLUORIDE EVOLUTION POINT)
4
PROPORTIONATING EQUIPMENT
FUEL AND COMBUSTION AIR
CLAY AND ROCK DRYER
(POTENTIAL FLUORIDE EVOLUTION POINT)
DRY MIXING AND BLENDING SILOS
TUBE MILL
VERTICAL MILL
FLUE GAS TO STACK
6
ROTARY KILN
3
GY
KILN FEED STORAGE
5
FUEL AND COMBUSTION AIR
CLINKER STORAGE
GYPSUM STORAG
CLINKER COOLER
(POTENTIAL FLUORIDE EVOLUTION POINT)
CEMENT STORAGE SILOS
FINISH MILL
7
PORTLAND CEMENT TO PACKING

A

O STACK
FLUORIDE
POINT)
3
GYPSUM
NKER
ORAGE
GYPSUM
STORAGE

BASIS: DRY PROCESS MANUFACTURE OF PORTLAND CEMENT

AT 10,000 BBL PER DAY

PROCESS STREAMS - TONS/DAY

Material	Stream Numbers						
	1	2	3	4	5	6*	7
HF				Amount Unknown		$0.008(g)^{(C)}$	
CaF_2 (Equiv.)	3.35(Est)	0.82 (Est)		"		$4.17(s)^{(C)}$	
Total Fluoride	3.35	0.82				4.17	
Total as F	1.63	0.40				2.03	
Limestone	$2500(s)^{(D)}$						
Shale (clay)		$620(s)^{(D)}$					
Gypsum			80(s)				
Fuel**							
Coal					$470(s)^{(D)}$		
Oil***					80,000(l) (A)		
Natural Gas****					$7,800(g)^{(D)}$		
Flue Gas****				$190,000(g)^{(E)}$		$270,000(g)^{(B)}$	
Flue particulates				$300(s)^{(E)}$		$215(s)^{(5)}$	
Portland Cement							$1880(s)^{*****(A)}$
Approx. Total Stream	2500	620	80	-	-	-	1880

* Gaseous Evolution Stream

** Coal, oil and natural gas fuel options are presented

*** Gal per day

**** SCFM (1 atm 60°F)

***** Equivalent to 10,000 bbl per day

Soluble fluoride evolution factor = 0.008 lb F/ton of cement (16 lb F/10^4 bbl of cement)

(A) Reference 2027
(B) Reference 4298
(C) Reference 4266
(D) Reference 4244
(E) Reference 2096

Figure 3-52. Dry Process Portland Cement Production — Uncontrolled Process Model

B

portland cement should reach 450 to 500 million barrels by 1975.(4292,4293) This would represent an increase of about 140 to 190 million barrels over the 1960 level, for an average annual increase of 2.5% to 3.0%. If these rates continued to the year 2000, the annual production would be 830 to 1050 million barrels (156 to 197 million tons). The 3% rate was assumed for the fluoride emission determination. Table 3-94 summarizes expected cement production levels.

3.10.4 Fluoride Emission Control Techniques

The particulate emission control technique currently employed in the cement industry is presented in Figure 3-53. This technique is effective in removal of particulates and the soluble fluorides absorbed thereon.

3.10.5 Fluoride Emissions

Cement production is of special interest since it involves evolution of fluorides in the presence of limestone. Information concerning the fate of the fluoride in this circumstance may be used to infer conclusions for similar situations, e.g., iron and steel processes or dry limestone process SO_2 control.

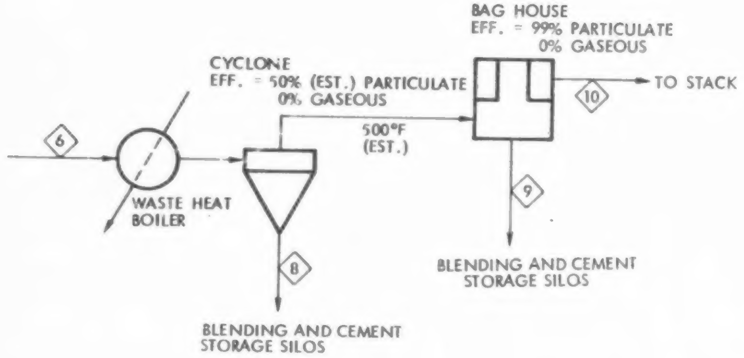
As noted earlier, the kilns are the major points of fluoride evolution in the cement process. At equilibrium, 100% of the charge fluoride would be evolved as gaseous HF at 2700°F (see Tables 3-95 and 3-96). At the same time as the gaseous HF is evolved, very large quantities of limestone and high free-lime-content particulate material are dispersed into the combustion product stream. The active alkaline surface area thus made available for adsorption and reaction with the evolved HF is enormous, and much of the evolved gaseous HF is removed from the gas stream.

Unfortunately, normal operating data are not available defining fluoride emission factors for cement production. The cement industry has concentrated on the particulate problem. Limited experience with fluorides added to the feed(4266) does indicate that: (1) 70 to 80% of the evolved fluoride can be collected in an electrostatic precipitator, and (2) gaseous and water soluble fluorides were only about 10% of the total

Table 3-94. Future Cement Production

	Actual 1964(4292)	Estimated 1975	Annual Growth Rate	Extrapolated to Year 2000
Cement Production				
Million Barrels	360	450(4292)	2.5%	830
(million tons)	(67.7)	(84.6)		(156)
	360	500(4293)	3.0%	1047
	(67.7)	(94.0)		(197)
	360	646(4293)	5.5(A)	2463
	(67.7)	(121.4)		(463)

(A) Reference (4293) indicates that this rate is probably far too optimistic.


6
WASTE HEAT BOILER
CYCLONE
EFF. = 50% (EST.) PARTICULATE
0% GASEOUS
8
BLENDING AND CEMENT STORAGE SILOS
500°F (EST.)
BAG HOUSE
EFF. = 99% PARTICULATE
0% GASEOUS
9
BLENDING AND CEMENT STORAGE SILOS
10
TO STACK

BASIS - WET AND DRY PROCESS MANUFACTURE OF PORTLAND CEMENT AT 10,000 BBL PER DAY

PROCESS STREAMS - TON/DAY

Material	Stream Number			
	6	8	9	10*
HF	0.008(g)			0.003(g)
CaF_2(equiv.)	4.17(s)	2.09(s)$^{(B,C)}$	2.06(s)$^{(B,C)}$	0.02(s)$^{(B,C)}$
Total Fluorides	4.17	2.09(s)	2.06	0.03
Total As F	2.03	1.02	1.01	0.018
Flue Gas**	270,000(g)			270,000(g)
Flue Particulates	202(s)***	101(s)$^{(B,C)}$	100(s)$^{(B,C)}$	1(s)$^{(B,C)}$
Approx. Total Stream	--	106	106	--

* Gaseous Effluent Stream
** SCFM (1 atm, 60°F)
*** Average value between wet and dry process (190 wet - 215 dry)

(A) Reflects an average fluoride content of the limestone and shale of 650 ppm with no fluorspar addition to the feed.
(B) Reference 2172
(C) Reference 2096

Source	Soluble Fluoride Emission Factor-lbF/ton Cement
Kiln Effluent	0.008
Assumed Fugitive Emission	0
Total Emission	0.003

Overall soluble fluoride emission factor for the industry = 0.008 lb F/ton cement (16 lb F/10^4 bbl cement)$^{(A)}$

Figure 3-53. Wet and Dry Process Portland Cement Production — Controlled Process Model

Table 3-95. Dry Cement Process Charge Composition

	Weight %	Mole %
SiO_2	0.175	0.082
Al_2O_3	0.045	0.012
Fe_2O_3	0.014	0.002
MgO	0.005	0.003
CaO	0.005	0.002
Na_2O	0.003	0.001
K_2O	0.009	0.003
$CaCO_3$	1.127	0.317
CaF_2	0.005	0.002
CH_4	3.515	6.187
N_2	72.100	72.519
O_2	22.081	19.433
H_2O	0.917	1.435

Fluoride Distribution
at 2700F

Product Compound	Concentration in Gas	% of Total Fluoride Charged
HF	40.0 ppm	100.

Table 3-96. Wet Cement Process Charge Composition

	Weight %	Mole %
SiO_2	0.154	0.072
Al_2O_3	0.040	0.011
Fe_2O_3	0.012	0.002
MgO	0.004	0.003
CaO	0.004	0.002
Na_2O	0.002	0.001
K_2O	0.008	0.002
$CaCO_3$	0.989	0.277
CaF_2	0.005	0.002
CH_4	3.483	6.102
N_2	72.028	72.115
O_2	21.767	19.069
H_2O	1.504	2.342

Fluoride Distribution
at 2700F

Product Compound	Concentration in Gas	% of Total Fluoride Charged
HF	40.0 ppm	100.

fluoride emissions. This would appear to verify the effectiveness of limestone, and possibly other particulate matter, in adsorbing or reacting with gaseous fluorides. The result is that alleviation of the particulate emission problem, which is being actively pursued, will also alleviate fluoride emission problems.

Assuming average fluoride content of limestone and shale (650 ppm F) with no fluorspar addition to feed, soluble fluoride emissions will grow from 270 tons (as F^-) in 1964 to 800 tons in 2000 if current control levels (no gaseous fluoride control) are maintained. If 99% efficient control systems are utilized, the emissions will decrease to less than 10 tons (as F^-) in 2000. Table 3-97 summarizes the emission data.

Table 3-97. Soluble Fluoride Emitted From The Cement Industry

	1964	2000
Cement Production (10^6 ton/year)	68	200
Soluble Fluoride Evolution Factor (lb F/ton cement)	0.008	0.008
Soluble Fluoride Emission Factor With Current Practice (lb F/ton cement)	0.008	0.008
Soluble Fluoride Emission Factor With 99% Control (lb F/ton cement)	--	0.00008
Soluble Fluoride Evolution (10^3 ton F/yr)	0.27	0.80
Soluble Fluoride Emission With Current Practice (10^3 ton F/yr)	0.27	0.80
Soluble Fluoride Emission With 99% Control (10^3 ton F/yr)	--	0.008

3.10.6 Economic Analysis

Basic Process

Table 3-98 presents the estimated economics for the production of portland cement by either wet or dry processes for three plant sizes. The extreme sensitivity of ROI to plant size is of interest--the estimated ROI's for the three plant sizes before installation of emission control are:

Plant Size Million bbls/year	ROI, %
1	3.1
4	18.8
8	33.5

Impact of Control

Table 3-99 indicates the estimated costs for the current emission control process used in both wet and dry methods of manufacture of portland cement. Impact on ROI for the 4 million barrel per year plant is approximately 18%.

Table 3-98. Estimated Economics of Portland Cement Manufacture(A)
(Pollution Control Cost Excluded)

	1.MM bbl/yr	4.MM bbl/yr	8.MM bbl/yr
Installed Capital Investment	8.0 $MM	25.0 $MM	35.2 $MM
Operating Costs			
Direct Costs			
Limestone (0.249 tons/bbl at 1.35$/ton)	0.34 $/bbl	0.34 $/bbl	0.34 $/bbl
Shale (0.062 tons/bbl at 2.00 $/ton)	0.12	0.12	0.12
Gypsum (0.008 tons/bbl at 2.00 $/ton)	0.02	0.02	0.02
Fuel (1.3 mm Btu/bbl at 0.35$/mm Btu)	0.46	0.46	0.46
Electric Energy (23 kwh/bbl at 0.007$/kwh)	0.16	0.16	0.16
Water (70 gal/bbl at 0.08$/gal)	0.01	0.01	0.01
Operating Labor(B)	0.58	0.20	0.13
Supervision and Fringe Benefits	0.58	0.20	0.13
Maintenance and Supplies (at 4% of invest./year)	0.32	0.25	0.18
Total Direct Costs	2.59	1.76	1.55
Indirect Costs			
Depreciation (at 5% per year)	0.40	0.31	0.22
Interest (at 7%, 20% Debt)	0.11	0.09	0.06
Insurance and Local Taxes	0.24	0.19	0.13
Overhead	0.69	0.24	0.15
Total Indirect Costs	1.44	0.83	0.56
Total Manufacturing Cost	4.03 $/bbl	2.59 $/bbl	2.11 $/bbl
General and Sales Expenses	0.08	0.05	0.04
F.o.b. Cost	4.11 $/bbl	2.64 $/bbl	2.15 $/bbl
Average Product Revenue	4.51 $/bbl	4.51 $/bbl	4.51 $/bbl
Profit After Taxes (taxed at 50%)	0.20 $/bbl	0.94 $/bbl	1.18 $/bbl
Cash Flow ($MM/year)	0.60 $MM/yr	5.00 $MM/yr	11.2 $MM/yr
Return on Investment(C)	3.1%	18.8%	33.5%

(A) Wet process plant; dry process costs are similar to wet process costs. Assumes 300 working days per year.

(B) Assuming 20, 28, 35 men/shift for the 1, 4 and 8 MM bbl/year plants, respectively.

(C) Assumes 80% equity funding.

Table 3-99. Portland Cement Production - Estimated Economics of Control Process Basis - 10,000 bbl Per Day of Portland Cement Produced

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	WASTE HEAT BOILER, 58,000 ft^2 t_{in} = 1500°F, t_{out} = 550°F, 1,250,000 cfm, $U\Delta t$ = 4800 Btu/hr/ft^2, low alloy steel, Q = 288 MM Btu/hr, 20 in W.G. pressure drop.	170.0	4383	3.64		619.0
2	CYCLONE, 524,000 cfm, 4.9 in W.G. pressure drop, carbon steel.	127.0	4387 4390 4392	2.98		379.0
3	BAGHOUSE, 498,000 cfm, 500°F, fabric filter, 2 in W.G. pressure drop.	168.0	4383	4.13		696.0
					Capital Subtotal	1,694.0
					Indirects (@ 15%)	254.0
					Contingency (@ 20%)	339.0
					Total Capital (as of January 1971)	2,287.0

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	27.49	0.11		27.60
2	2.82	0.13		2.95
3.	1.10	1.26		2.36
Subtotal				32.91
Water[21]				-
Disposal[22]				-
Total Operating Cost				32.91

Total Operating Cost ($/hr)	32.91
Taxes and Insurance (2%, 300 days)	6.35
Capital (6.7%, 300 working days)	21.28
Pollution Control Cost ($/hr)	60.54
Pollution Control Cost ($/bbl)	0.15

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

3.11 HF ALKYLATION PROCESSES

3.11.1 General

Alkylation is a process for reacting isoparaffins with olefins or olefin mixtures to form highly branched, high octane, paraffinic products. The major currently used alkylation processes utilize either sulfuric acid or hydrofluoric acid as a catalyst. Of the total U.S. alkylate production (775,000 bbl/day in 1970), about 30% (236,000 bbl/day) was produced in 62 units utilizing the HF process.(4238) The units varied in capacity from 500 to 14,500 bbl/day with the average plant being 3800 bbl/day.(4238)

3.11.2 Industry Description

A simplified flow diagram and fluoride mass balance of the HF alkylation process is presented in Figure 3-54. It is estimated that 75% of the producing refineries burn the acid residue (stream 3) while the remaining 25% treat this stream as discussed later in this section. This estimation is based on the assumption that only those units located in high density urban areas utilize the control process.

3.11.3 Production Trends

Demand for petroleum products has been steadily increasing from 10.6 million bpd in 1963 to 13.0 million bpd in 1970. It is expected that demand will reach 15 million bpd in 1975.(4294) This is equivalent to a growth rate of about 2.7% per year in contrast to the 3% experienced since 1955 and the 5.5% rate from 1945 to 1955. Rapid growth in passenger vehicle and freight mileage over the next 10 or 15 years will create a large absolute demand for gasoline and probably boost the annual rate of increase to about 3.5%. In contrast to the high rates of growth experienced in the past, however, the outlook is for an increase in demand for gasoline and for total refined products more closely geared to the rate of growth of U.S. economic activity.

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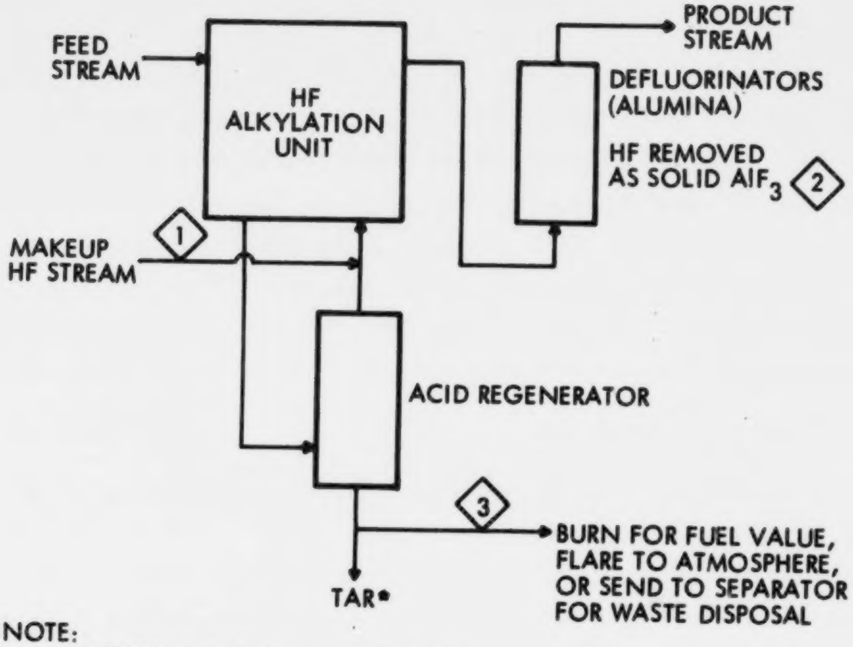

FEED STREAM
HF ALKYLATION UNIT
PRODUCT STREAM
DEFLUORINATORS (ALUMINA)
HF REMOVED AS SOLID AlF_3
2
1
MAKEUP HF STREAM
ACID REGENERATOR
3
BURN FOR FUEL VALUE, FLARE TO ATMOSPHERE, OR SEND TO SEPARATOR FOR WASTE DISPOSAL
TAR*

NOTE:

*THIS TAR STREAM IS VERY SMALL (~ 0.4 BBL/DAY) FOR AN AVERAGE UNIT. (4271)

Basis: 3800 bpd Production Unit (Fluoride Balance Only)

Process Streams - Tons/Year$^{(A)}$

Material	Stream Number		
	1	2	3*
HF	125$^{(B)}$		122$^{(B)}$
HF Equivalent		2.5$^{(B)}$	
Total Fluoride	125	2.5	122
Total as F	119	2.4	116

*Gaseous effluent stream

Soluble fluoride evolution factor = 0.18 lbF/bbl alkylate

(A) Assumes 330 operating days/year

(B) References 4239, 4240, 4241

Figure 3-54. Simplified HF Alkylation - Uncontrolled Process Model

Total alkylate production in March 1971 was 775,000 bpd of which 236,000 bpd (30.4%) was produced by the HF alkylation process.(4295) If a 2.5% growth rate is assumed, the production rate (via HF alkylation) will be 643,000 bpd in 2000. These data are presented in Table 3-100.

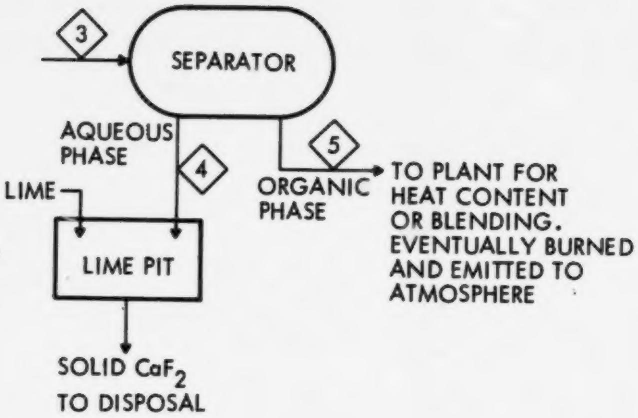
Table 3-100. HF Alkylation Projection

	1971(4295)	Estimated Rate of Increase*	Estimated Year 2000 Production
Alkylate Produced Utilizing HF Catalyzed Process (10^3 bpd)	236	2.5%	643

*Estimation is highly questionable because of possible changes in energy sources for future transportation and octane requirements if the source of energy is gasoline.

3.11.4 Fluoride Emission Control Techniques

The HF content of product streams is removed by passing those streams through defluorinating towers packed with alumina. The fluoride is then removed from the system and disposed of as AlF_3,(4240,4241) a solid that is readily recovered, and easily sold. The bottoms product from the acid regeneration unit which contains the bulk of the fluoride (98%) is sent to a separator. The aqueous phase, containing about 70% of the HF (~16 tons/day on an industry basis) is generally pumped to a lime pit where the fluoride is converted to CaF_2 and disposed of in that form.(4241) The remainder of the HF in the acid regenerator bottoms product leaves the system in the organic phase from the separator.(4241) This organic liquid containing approximately 7 tons/day fluoride (on an industry basis) is either used for fuel value in reboilers or furnaces at the refinery or blended into various product streams.(4240,4241) In either case, this fluoride (from the organic phase) is eventually emitted to the atmosphere. A process flow diagram and mass balance are presented in Figure 3-55. Since no definitive data could be found regarding the degree of control utilized throughout the industry, it was estimated that 25% of the production utilized lime pit disposal.


3
SEPARATOR
AQUEOUS PHASE
4
LIME
LIME PIT
5
ORGANIC PHASE
TO PLANT FOR HEAT CONTENT OR BLENDING. EVENTUALLY BURNED AND EMITTED TO ATMOSPHERE
SOLID CaF_2 TO DISPOSAL

Basis: 3800 bpd Production Unit (Fluoride Balance Only)

Process Streams - Tons/Year(A)

Material	Stream Number		
	3	4	5*
HF	122(C)	86(B)	36(B)
Total as F	116	82	34

*Gaseous effluent stream

(A) Assumes 330 operating days/year

(B) Reference 4241

(C) References 4239,4240,4241

(D) Estimate usage of control process on 25% of production (based on facilities located in high density urban areas)

Source	Soluble Fluoride Emission Factor lbF/bbl Alkylate
Control Process	0.05
Assumed Fugitive	0
Total Emission	0.05

Overall soluble fluoride emission factor(D) = 0.15 lbF/bbl Alkylate

Figure 3-55. HF Alkylation - Controlled Process Model

3.11.5 Fluoride Emissions

Various sources of information indicate the levels of HF consumption or loss to be in the range of 0.05 to 0.8 pound acid (4239, 4240,4241) per barrel of alkylate produced. It was found that most producers assume 0.21 pound acid per barrel of alkylate to be the correct value for most currently operated large units.(4241) This corresponds to a total industry HF consumption (or loss) of 23.6 tons/day. Industry sources(4240,4241) indicate that approximately 2% of this amount (0.6 ton/day) is lost to the product stream while the remaining 98% (23.0 tons/day) exits the processes as a bottoms product from the HF acid regeneration units. This bottoms product is either flared directly, burned for fuel value or sent to a separator. In the latter case the organic phase is recycled, and the aqueous acid phase sent to lime pits for disposal. The fluorides contained in the product gasoline (200 tons per year) are discharged, as the result of combustion, in the form of HF.

Current industry practice produced soluble fluoride emissions at the refineries of 5800 tons in 1971 and will produce 15,900 tons (as F) in 2000 if current abatement procedures are followed.* If 99% efficiency control devices are utilized industry-wide, the 2000 projection is 190 tons. These data are presented in Table 3-101.

3.11.6 Economic Analysis

Basic Process

Table 3-102 presents estimates of the current economics of production of alkylate by the use of HF. Return on investment is estimated as ranging from a negative value to 8.3%. The systems operate at a loss except for the 5000 bpd facility.

Impact of Control

Table 3-103 presents estimates of the cost of control of lfuoride emissions from HF alkylation.

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*Assumes that 25% of production utilizes lime pits for partial control acid wastes.

Table 3-101. Soluble Fluoride Emissions from HF Alkylation

	1971	2000
HF Catalyzed Alkylate Production (10^3 bpd)	236	643
Soluble Fluoride Evolution Factor (lbF/bbl Alkylate)	0.18	0.18
Soluble Fluoride Emission Factor with Current Control (lbF/bbl Alkylate)*	0.15	0.15
Soluble Fluoride Emission Factor with 99% Control (lbF/bbl Alkylate)	–	0.0018
Soluble Fluoride Evolved (10^3 tons F/year)	7.0	19.0
Soluble Fluoride Emissions with Current Practice (10^3 tons F/year)	5.8	15.9
Soluble Fluoride Emissions with 99% Control (10^3 tons F/year)	–	0.19

*Estimated usage of control process is 25% of production (based on facilities located in high population density urban areas).

Table 3-102. Estimated Economics of HF Alkylation Units (Pollution Control Cost Excluded)

	Plant Capacity (bpd)		
	500	3800	5000
Total Capital Investment	0.5 $MM	1.3 $MM	1.5 $MM
Operating Costs			
Direct Costs			
Olefin Feed (1.1 bbl olefin/bbl Alkylate @ \$3.00/bbl)	3.30 \$/bbl Alk.	3.30 \$/bbl Alk.	3.30 \$/bbl Alk.
Hydrogen Fluoride (0.2 lbs H_2F_2/bbl Alkylate @ \$.40/lb)	0.08	0.08	0.08
Alumina (0.004 lbs Al_2O_3/bbl Alkylate @ \$0.10/lb)	(a)	(a)	(a)
Steam (700 lbs/bbl Alkylate at \$0.45/1000 lbs)	0.32	0.32	0.32
Electricity (5.8 kwh/bbl @ \$0.007/kwh)	0.04	0.04	0.04
Labor (0.14, 0.1 and 0.09 man-hr/bbl @ \$5.00/man-hr)	0.70	0.50	0.45
Supervision and Fringe Benefits	0.70	0.50	0.45
Maintenance and Supplies	0.18	0.06	0.05
Total Direct Costs	5.32	4.80	4.69
Indirect Costs			
Depreciation	0.30	0.10	0.09
Interest (at 7%, 20% Debt)	0.02	0.01	0.01
Taxes and Insurance	0.04	0.03	0.03
Plant and Labor Overhead	0.84	0.60	0.54
Total Indirect Costs	1.20	0.74	0.67
N-Butane Credit (8 lbs/bbl Alkylate at 0.01 \$/lb)	(0.08)	(0.08)	(0.08)
Manufacturing Cost	6.44	5.46	5.28
General and Sales Expenses	0.13	0.11	0.11
FOB Cost	6.57	5.57	5.39
Product Revenue	5.50	5.50	5.50
Profit After Tax (@ 50% tax)	(1.07)	(0.07)	0.06
Cash Flow (\$1000/year)	(127)	38	239
ROI (%)	---	---	8.3

(a) \$1100/year or 0.0009 \$/bbl
(b) Assumes 80% equity Funding

Table 3-103. HF Alkylation - Estimated Economics of Control Process
Basis - 3800 bpd of alkylate produced.

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	SEPARATOR, 0.5 lb HF/min, 8 bpd, 0.1 lb hydrocarbons/min, 100 gal capacity, neoprene lined steel	2	4383	1.50		3
2	LIME PIT, 5000 gal capacity, 0.36 lb HF/min, neoprene lined steel	10	4383	1.50		15
					Capital Subtotal	18
					Indirects (@ 15%)	3
					Contingency (@ 20%)	4
					Total Capital (as of January 1971)	25

Operating Cost ($ / hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.05	0.15		0.20
2	0.05	0.38		0.43
Subtotal				0.63
Water(21)				--
Disposal(22) (1 bbl tar/day)				0.08
$CaCO_3$ (100 lb/hr @ $3.00 ton)				0.15
Total Operating Cost				0.86

Total Operating Cost ($/hr)	0.86
Taxes and Insurance (2%, 330 days)	0.06
Capital (9.0%, 330 working days)	0.28
Pollution Control Cost ($/hr)	1.20
Pollution Control Cost ($/bbl)	0.01

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

3.12 HF PRODUCTION

3.12.1 General

Manufacturing processes for fluorine, hydrogen fluoride, and derivative chemicals differ in two important respects from all other processes discussed in this report. First, the fluorine involved is a portion of both raw material and product. This creates an economic incentive to minimize fluoride losses. Second, the quantity and concentration of toxic fluorides constitutes a potential hazard which requires treatment to preclude adverse legal and regulatory action.

3.12.2 Industry Description

Figure 3-56 presents a flow schematic(4276,4242,4223,4261) and mass balance for the production of HF at the rate of 25 tons per day (50% anhydrous HF, 25% each of 50% and 80% HF).

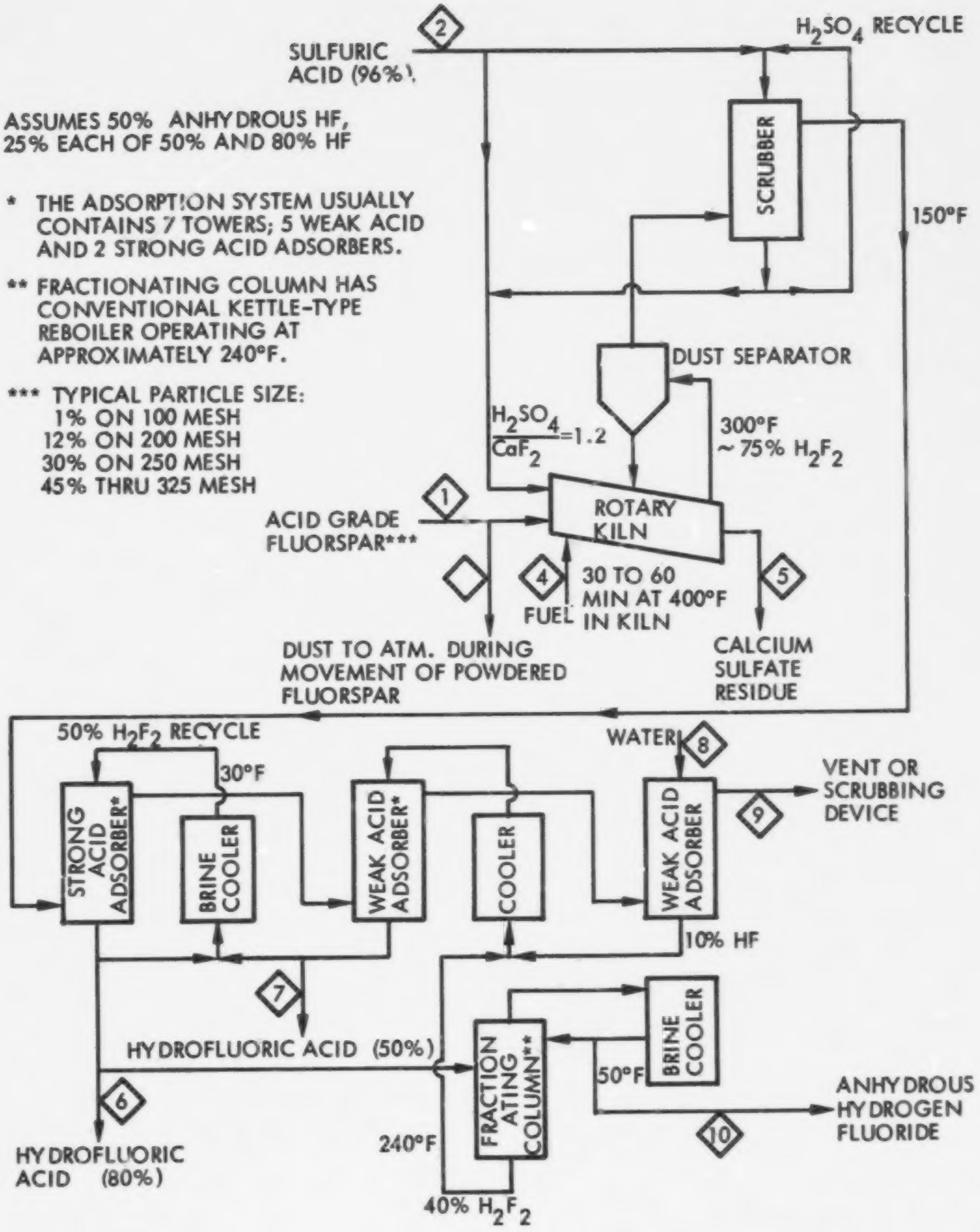
3.12.3 Production Trends

The historical growth of HF production has been 7.8% annually for the period 1959 to 1969.(4296) HF consumption for aluminum fluoride and synthetic cryolite production (used in manufacture of aluminum) plus the growing fluorocarbon market will tend to keep HF demand high. Expected growth rates between 5% and 7% are seen during the next few years.(4296) If these rates are extrapolated to the year 2000, HF production (as anhydrous HF) will increase from 337,000 tons in 1970 to between 1,430,000 and 2,565,000 tons.

3.12.4 Fluoride Emission Control Techniques

Hydrofluoric acid plant stack gas control systems are normally integral with the manufacturing process. Collection and transport systems are in-line extensions of the production system to the fluoride effluent control system. The spent charge from the kiln must be treated properly to prevent evolution of residual HF, but collection systems are not typically used for control of spent charge emissions.

Figure 3-57 presents a typical control installation using water scrubbing for a 25 ton per day plant. Either wet or caustic scrubbers are added as a final plant stage to act as a final HF removal step.


SULFURIC ACID (96%)
2
H_2SO_4 RECYCLE
SCRUBBER
150°F
DUST SEPARATOR
$\frac{H_2SO_4}{CaF_2}=1.2$
300°F
~ 75% H_2F_2
1
ACID GRADE FLUORSPAR***
ROTARY KILN
4
FUEL
30 TO 60 MIN AT 400°F IN KILN
5
CALCIUM SULFATE RESIDUE
DUST TO ATM. DURING MOVEMENT OF POWDERED FLUORSPAR
50% H_2F_2 RECYCLE
30°F
WATER
8
STRONG ACID ADSORBER*
BRINE COOLER
WEAK ACID ADSORBER*
COOLER
WEAK ACID ADSORBER
9
VENT OR SCRUBBING DEVICE
10% HF
7
HYDROFLUORIC ACID (50%)
6
HYDROFLUORIC ACID (80%)
FRACTIONATING COLUMN**
BRINE COOLER
50°F
240°F
40% H_2F_2
10
ANHYDROUS HYDROGEN FLUORIDE

ASSUMES 50% ANHYDROUS HF, 25% EACH OF 50% AND 80% HF

* THE ADSORPTION SYSTEM USUALLY CONTAINS 7 TOWERS; 5 WEAK ACID AND 2 STRONG ACID ADSORBERS.

** FRACTIONATING COLUMN HAS CONVENTIONAL KETTLE-TYPE REBOILER OPERATING AT APPROXIMATELY 240°F.

*** TYPICAL PARTICLE SIZE:
1% ON 100 MESH
12% ON 200 MESH
30% ON 250 MESH
45% THRU 325 MESH

BASIS - 25 TONS/DAY
PROCESS STRE

Material
HF
SiF_4
CaF_2
Total Fluorides
Total as F
$CaCO_3$
SiO_2
S
H_2SO_4 (96%)
$CaSO_4$
CO_2
SO_2
H_2O
Fuel
Approx. Total Stream

*Gaseous effluent stream

(A) Impurities in the fl

(B) The calcium sulfate

(C) References 42 , 42

(D) Reference 4261

Soluble fluoride evoluti

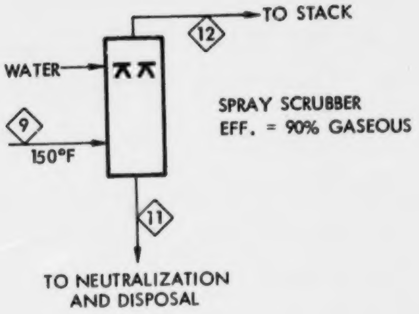
A

25 TONS/DAY HF PRODUCTION (ASSUMES 50% ANHYDROUS HF, 25% EACH OF 50% AND 80% HF)
PROCESS STREAMS -LBS/HR

	Stream Numbers									
	1	2	3	4	$5^{(B)}$	6	7	8	9^{*}	10
						510 (1)	510 (1)		$26\ (g)^{(D)}$	$1010(C)$
									$34\ (g)^{(D)}$	
	$4100(s)^{(C)}$		$20(s)^{(D)}$		$40(s)^{(C)}$					
s	4100		20		40	510	510		60	1010
	2000		10		20	480	480		50	960
	$40^{(A)}$									
	$40^{(A)}$				20					
	$2^{(A)}$									
%)		5400								
					7100					
									16(g)	
	$4^{(A)}$					130	510	400	3(g)	
				7×10^{6}BTU						
	4200	5400	20	--	7100	640	1000	400	80	1010

ent stream
in the fluorspar feed.
um sulfate residue stream may liberate fluorides. Literature search revealed no data.
s 4242, 4259
4261
de evolution factor = 52 lb F/ton HF

Figure 3-56. Hydrofluoric Acid Production - Uncontrolled Process Model


TO STACK
12
WATER
9
150°F
SPRAY SCRUBBER
EFF. = 90% GASEOUS
11
TO NEUTRALIZATION
AND DISPOSAL

BASIS - 25 TONS/DAY HF PRODUCTION
(ASSUMES 1/2 ANHYDROUS HF, 1/4 50% HF AND 1/4 80% HF PRODUCED)

PROCESS STREAMS - LB/HR

	Stream Number		
Materials	9	11	12*
HF	26(g)	24(g)	2(g) (Est.)
SiF_4	34(g)	31(g)	3(g) (Est.)
Total Fluorides	60	55	5
Total as F	50	46	4
CO_2	16(g)		16(g)
H_2O	3(g)	2.5 (al)$^{(A)}$	0.5(g)
Approx. Total Stream	80	60$^{(A)}$	20

*Gaseous Effluent Stream

(A) Plus scrubbing water.

(B) Assumes 100% usage of scrubbers on all facilities.

Source	Soluble Fluoride Emission Factor - lb F/ton HF
Scrubber	4.1
Assumed Fugitive	0.0
Total Emission	4.1

Overall soluble fluoride emission = 4.1 lb F/ton HF$^{(B)}$

Figure 3-57. HF Production - Controlled Process Model

3.12.5 Fluoride Emissions

Soluble fluoride emissions will increase from 700 tons (as F) in 1970 to about 5330 tons in 2000 at current abatement levels. If 99% control devices are employed, the fluoride emission will drop to 680 tons in the year 2000. These data are summarized in Table 3-104.

3.12.6 Economic Analysis

Table 3-105 presents the estimated economics of HF production at three plant capacities (5, 25, and 80 tons per day). Returns on investment for the three plants prior to the use of fluoride controls are 0.5%, 32.5% and 58.1%, respectively.

3.12.7 Impact of Control

Table 3-106 indicates the estimated costs of fluoride pollution control for a 25 ton per day plant. Impact on ROI is estimated as a ΔROI of about -0.5% for the 25 ton per day plant size.

Table 3-104. Soluble Fluoride Emissions from HF Production

	1970	2000
HF Production (10^6 tons/year)	0.34	2.60
Soluble Fluoride Evolution Factor (lb F/ton HF)	52	52
Soluble Fluoride Emission Factor with Current Practice (lb F/Ton HF)	4.1	4.1
Soluble Fluoride Emission Factor with 99% Control (lb F/ton HF)	--	0.52
Soluble Fluroide Evolution (10^3 tons F/year)	8.84	67.6
Soluble Fluoride Emission with Current Practice (10^3 ton F/year)	0.70	5.33
Soluble Fluoride Emission with 99% Control (10^3 ton F/year)	--	0.68

Table 3-105. Estimated Economics of Hydrofluoric Acid Production (excluding pollution control cost)

	Plant Capacity		
	5 Tons/Day	25 Tons/Day	80 Tons/Day
Capital Investment			
Installed Capital[(A)]	1.4 \$MM	3.2 \$MM	6.9 \$MM
Off Sites	0.6	1.3	2.8
Total Capital Investment	2.0	4.5	9.7
Production Costs			
Direct Costs			
Fluorspar (acid grade: 2.02 tons/ton 100% H_2F_2 at 56.39)	113.91 \$/ton H_2F_2	113.91 \$/ton H_2F_2	113.91 \$/ton H_2
Sulfuric Acid[(B)] (2.0 tons 100%/ton 100% H_2F_2 at \$12.86 \$/ton)	25.72	25.72	25.72
Fuel (6720 std. cu ft/ton 100% H_2F_2 at \$0.35/1000 std ft^3)	2.35	2.35	2.35
Water (2200 gal/ton 100% H_2F_2 at \$0.40/10^3 gal)	0.88	0.88	0.88
Electric Power (450 kwh/ton 100% H_2F_2 at 0.007 \$/kwh)	3.15	3.15	3.15
Operating Labor (4 men/shift)	76.80	15.36	4.80
Supervision and Fringe Benefits	38.40	7.68	2.40
Maintenance and Supplies	18.32	7.93	4.58
Total Direct Cost	279.53	176.38	157.07
Indirect Costs			
Depreciation (at 10%)	121.21	54.55	36.74
Interest (at 7%, 20% Debt)	16.97	7.64	5.14
Local Taxes and Insurance	30.30	13.64	9.19
Plant and Labor Overhead	92.16	18.43	5.76
Total Indirect Costs	260.64	94.26	56.83
Total Manufacturing Cost (\$/ton 100% H_2F_2)	540.17	270.64	213.89
General and Sales Expenses (\$/Ton 100% H_2F_2)	10.80	5.41	4.28
FOB Cost (\$/Ton 100% H_2F_2)	550.97	276.05	218.17
Product Revenue (\$/ton 100% H_2F_2)	560.00	560.00	560.00
Profit After Taxes (at 50%)	4.52 \$/ton H_2F_2	141.98 \$/ton H_2F_2	170.92 \$/ton H_2F_2
Cash Flow (\$MM/yr)	0.21 \$MM/yr	1.6 \$MM/yr	5.5 \$MM/yr
Return on Investment[(C)]	0.5%	32.5%	58.1%

(A) Capital for sulfuric acid plant not included.

(B) Sulfuric acid plant collocated.

(C) Assumes 80% equity funding.

Table 3-106. Hydrofluoric Acid Production-Estimated Economics of Control Process

Basis - 25 tons per day of HF (assumes 50% anhydrous HF and 25% each of 50% and 80% HF produced.

Capital Cost Estimates ($1000)

Item Number	Description	Equipment F.O.B. Cost	Reference Number	Installation Factor		Equipment Installation Cost
1	SPRAY SCRUBBER, 1 ft - 6 in. diameter by 8 ft, monel clad, 50 ft^3/min, 8 ft/sec max velocity, 2 gal/min, 2 in W.G.	5	4383 4391 4392	1.77		8
				Capital Subtotal		8
				Indirects (@ 15%)		1
				Contingency (@ 20%)		2
				Total Capital (as of January 1971)		11

(a) $/ton HF

All control economics footnotes are located in Section 3.1.1, pages 3-10 and 3-11.

Operating Cost ($ /hr)

Item Number	Power Cost	Maintenance Cost		Equipment Operating Cost
1	0.01	0.25		0.26
Subtotal				0.26
Water[21] (2 gpm, 0 recycle)				0.01
Disposal[22]				----
Total Operating Cost				0.27

Total Operating Cost ($/hr)	0.27
Taxes and Insurance (2%, 330 days)	0.03
Capital (9.1%, 330 working days)	0.13
Pollution Control Cost ($/hr)	0.43
Pollution Control Cost(a) ($/ton)	0.41

3.13 NONFERROUS METALS SMELTING AND REFINING INDUSTRY

3.13.1 General

The nonferrous metals smelting and refining industry produces copper, lead and zinc by thermal processing of the metal ores. Most of the ores processed in the U.S. are sulfide mineral concentrates, separated by various roughing and flotation techniques from a wide range of gangue minerals. The separation is of necessity incomplete, and a portion of the gangue minerals accompanies the sulfide minerals through the thermal processing. The gangue minerals frequently contain inorganic fluorides (Table 3-107*). These fluorides are evolved as gaseous HF in the high temperature zones - the copper reverberatory furnaces, lead refining kettles, and zinc sintering machines and roasting furnaces - where temperatures range from 1400° to 2400°F, and more than sufficient combined hydrogen to satisfy the stoichiometry of the reaction is present. There is currently no information available in the open literature on the fluoride contents of the various ores and concentrates, and no data has been published on fluoride emissions from U.S. smelters.

Sixteen of the 37 American copper, lead and zinc smelters have by-product sulfuric acid plants(4271) abating sulfur oxide emissions on portions of the smelter effluent stack gases. Each of these plants has a humidifying tower, cooling tower and mist precipitator, where the hot smelter exit gases are treated to lower the gas temperature and remove the excess moisture and mist load. Theoretically, most of the fluorides fed to the acid plant should be removed in these devices. Practically, the presence of weak H_2SO_4 and SO_2 in the solution will raise the partial pressure of the HF sufficiently so that less than maximum removal will take place.

Because of the uncertainties associated with fluoride emission quantities in the nonferrous metal smelting and refining industry, no economic analyses have been made of production costs for the industry. Since there are no current processes used for fluoride emission control, no analyses have been made of control costs.

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*Table 3-107 appears at the end of Section 3.13

3.13.2 Copper Smelting and Refining Industry

Copper bearing ore bodies are associated with a wide range of fluoride containing minerals. The fluoride containing minerals vary widely in F content and in distribution through the ore body. Concentration by flotation does not separate the copper sulfide ore completely from any associated fluoride minerals. Detailed analyses of the various ores and concentrates produced in the U.S. are needed; these data are not available in the literature.

Industry Description. The primary copper minerals are chalcocite (Cu_2S - 79.8% Cu), chalcopyrite ($CuFeS_2$ - 34.6% Cu), bornite (Cu_3FeS_3 - 55.5% Cu) and covellite (CuS - 66.5% Cu). These occur in copper-bearing ore bodies containing varied gangue minerals - typical ore bodies are copper-bearing sulphides chiefly chalcopyrite or lean, copper-bearing pyrite in igneous rocks; irregular masses of copper-bearing sulphides in contract zones, associated with lime silicates; veins along faults, with greater or less replacement and impregnation of the walls; lenticular or pod-shaped bodies of pyrite or pyrrhotite, with chalcopyrite.

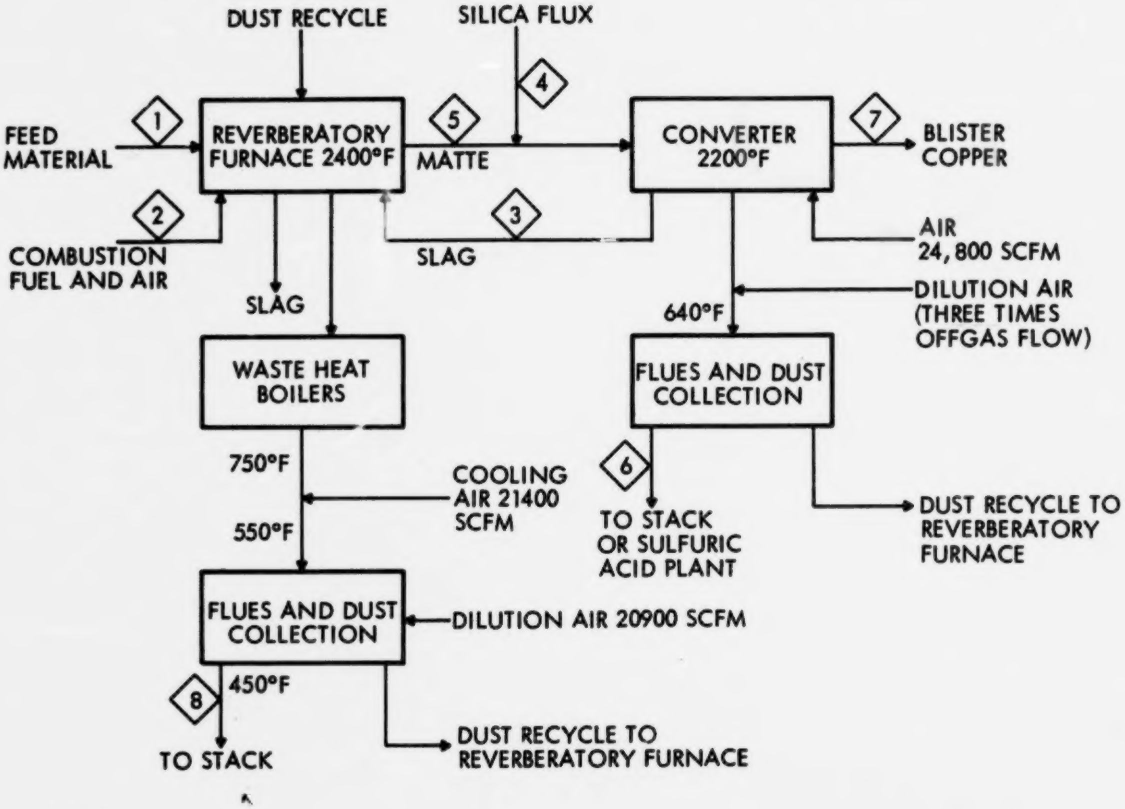
The industry typically concentrates as-mined ores by crushing, grinding and flotation. The grind is kept at 60 mesh with rougher and cleaning flotation. Carryover of fluoride-bearing minerals would depend on their flotation characteristics as compared to the ore.

Ore concentrates may be fed either to a roaster, or as in Figure 3-58, directly to a reverberatory furnace for smelting. Figure 3-58 gives the process model and mass balances for a typical 230-ton (blister copper) per day plant.

If roasting is employed, this first stage of the smelting process operates at temperatures of about 1200°F. Little fluoride is volatilized in this stage.

The reverberatory furnace melts the metal-bearing change and forms the matte and slag. Typical operating conditions for the "reverbs" are:(4271)

Furnace bath temperature	2400°F
Dust load in offgas	2-5 grains/scf
SO_2 in offgas	0.5-3.5%


DUST RECYCLE
SILICA FLUX
FEED MATERIAL
1
REVERBERATORY FURNACE 2400°F
5
MATTE
4
CONVERTER 2200°F
7
BLISTER COPPER
2
COMBUSTION FUEL AND AIR
SLAG
3
SLAG
AIR 24,800 SCFM
DILUTION AIR (THREE TIMES OFFGAS FLOW)
640°F
WASTE HEAT BOILERS
FLUES AND DUST COLLECTION
750°F
COOLING AIR 21400 SCFM
550°F
6
TO STACK OR SULFURIC ACID PLANT
DUST RECYCLE TO REVERBERATORY FURNACE
FLUES AND DUST COLLECTION
DILUTION AIR 20900 SCFM
450°F
8
TO STACK
DUST RECYCLE TO REVERBERATORY FURNACE

NOTE:

COPPER SMELTING PROCESS MODEL B (4271) WHICH INCLUDES A "ROASTER" AHEAD OF THE "REVERBERATORY FURNACE," HAS ALMOST ALL FLUORIDE EVOLUTION FROM THE REVERBERATORY FURNACE,* AND THE SOLUBLE F EMISSION FACTOR IS IDENTICAL WITH THAT OF PROCESS MODEL B.

* TRW SYSTEMS ESTIMATE

Material
HF
CaF_2
Total fluorides
Total as F
Cu
Fe
S
SiO_2
CaO
Al_2O_3
Other
Water
Air
Natural Gas
Approx. Total Str

Soluble F emissio

(A) SCFM (32°F,
(B) TRW estimate

*Gaseous effluent

A

Basis: Smelter Capacity of 230 Tons/Day of Blister Copper
Process Stream - Tons/24-Hour Day

aterial	Stream Number 1	2	3	4	5	6	7	8*
								$0.09^{(g)(A)}$
	$0.18^{(s)(B)}$				$0.00^{(B)}$		$0.00^{(B)}$	—
luorides	0.18				$0.00^{(B)}$		$0.00^{(B)}$	$0.09^{(g)(B)}$
s F	0.09				$0.00^{(B)}$		$0.00^{(B)}$	$0.09^{(g)(B)}$
	234		23	0.7	253	$0.7^{(s)}$	230	$0.4^{(s)}$
	228		227	15	212	$0.7^{(s)}$		$0.4^{(s)}$
	258		4.4	0.2	163	$159^{(g)}$	0.2	$85^{(g)}$
	92		190	185	6.4	$0.9^{(s)}$		$0.5^{(s)}$
	45		5.6	4.3	1.3	—		$0.1^{(s)}$
	30		8.7	8.7	—	—		
	79		72	3.3	3.8	$2.5^{(s)}$		1.5
	91		—					
		$36200^{(A)}$				$64800^{(A)}$		$90800^{(A)}$
l Gas		$2800^{(A)}$						
Total Stream	1056	$39000^{(A)}$	530	217	640	$64800^{(A)}$	230	$90800^{(A)}$

F emission factor = 0.78 lb/ton blister copper produced

M (32°F, 1 atm)

estimate, in the absence of any reported data

effluent stream

B

Figure 3-58. Copper Smelting - Uncontrolled Process Model A(4271)

The fluoride contained in the charge is evolved as HF under these conditions, at equilibrium. The molten matte produced in the reverberatory furnace is transferred to the converters whose function is to oxidize and and separate the iron and sulfur from the matte. The oxidation reaction is sufficient (when air blown) to maintain the converter at approximately 2250°F. SO_2 is emitted with the other flue gases. Silica flux is added to combine with the iron oxide to form a fluid iron silicate slag.

Production Trends. Current (1967) copper metal production is 1.628 million tons per year. Assuming a 3% annual increase in production, copper metal production in 2000 would be 4.2 million tons.

Fluoride Emissions. Because of the total lack of data in the literature, it was necessary to estimate first the "average" fluoride content of the concentrate fed to U.S. copper smelters; then, from this information, the fluoride evolved in the reverberatory furnaces; and finally the portion of the evolved fluorides captured in the by-product sulfuric acid plant. The average copper mineral content (Cu, S and Fe) of ore concentrates was estimated at 83.5%. The remaining 16.5% of the concentrates is gangue minerals, with an estimated 650 parts per million of fluoride.* Based on these assumptions, and those noted above, soluble fluoride emissions are estimated at 634 tons annually for 1967, and projected to be 1638 tons in 2000 if current lack of control continues.

Fluoride Emission Control Techniques. There are no fluoride emission control techniques currently employed in the industry.

3.13.3 Lead Smelting and Refining Industry

The major lead ore bodies are associated with a wide range of fluoride containing minerals which include fluorite. The fluoride containing minerals vary widely in distribution through the ore bodies. Concentration by roughing and cleaning flotation does not entirely separate the economic mineral from the associated gangue minerals, including the fluoride minerals. As with copper, detailed analyses of the various ores and concentrates produced in the U.S. are needed and are not available in the literature.

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*Based on the average fluoride content of the earth's crust (Ref. 4242)

Industry Description. The primary economic lead mineral is galena (PbS - 86.6% Pb). Other lead minerals, of secondary importance, are cerussite ($PbCO_3$ - 77.5% Pb); anglesite ($PbSO_4$ - 68.3%); and pyromorphite ($3\ Pb_3(PO_4)_2 \cdot PbCl_2$ - 76.2% Pb).

Galena comprises the vast majority of the ore mined. There are three general classes of lead ore: (a) those containing lead alone as an economic metal, (b) lead-zinc ores, (c) lead-silver ores; calcite, dolomite and pyrite are the common gangue minerals of the first two classes, quartz of the third class.

Concentration is normally accomplished by crushing, grinding (a gravity separation is sometimes used at this stage) and, finally, by a series of roughing and cleaning flotation steps. The concentrate consists generally of the following range of compositions:

Component	Quantity, %
Pb	55 to 70
Zn	Up to 6.5
Cu	0.5 to 4.0
S	13 to 18.5
Fe	Up to 5
Silica, lime, cadmium	Minor amounts
silver, gold, arsenic, fluorine	

The first operation in lead smelting is sintering which roasts the ore to remove the sulfur and at the same time produces a strong porous mass suitable for the blast furnace. Silica and limestone are added as fluxes which control the proportion of the sulfur in the mix and thus keep the temperature below 1400°F. Some 85% of the sulfur is eliminated in this step, 14% remains in the slag and other solid by-products and 1% is eliminated by the blast and the dross furnaces.

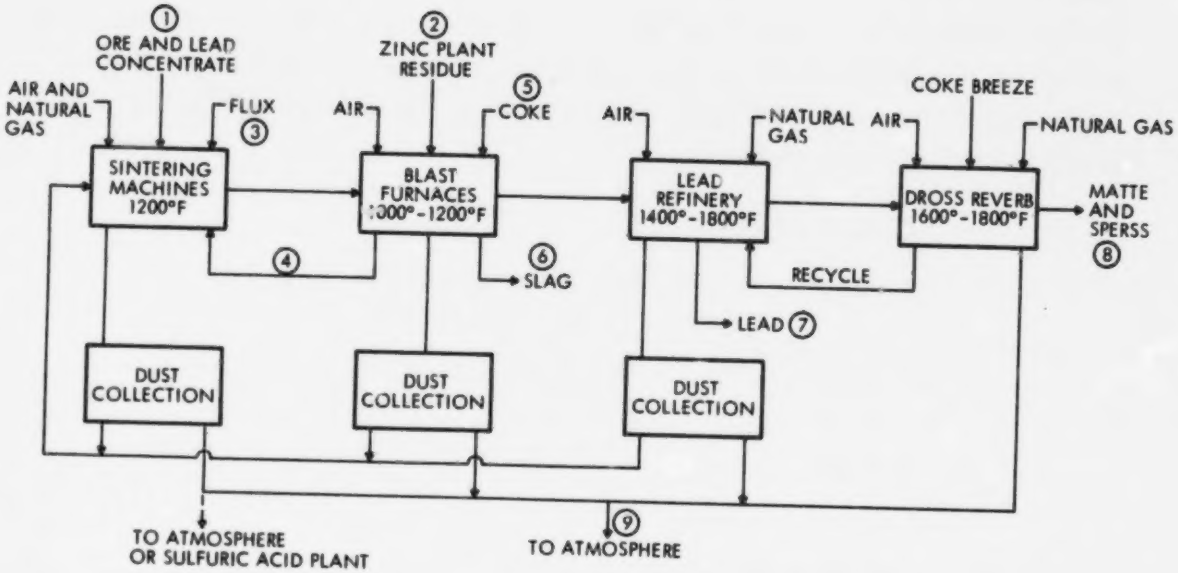
The purpose of the blast furnace is to reduce the lead oxide to lead by carbon monoxide produced from coke added to the furnace. The furnace temperature ranges from 1000° to 1200°F. Dust from this operation is collected in a baghouse, and SO_2 in the flue gas ranges from 0.01 to 0.25%. Some flux (silica or limestone) may be added to the furnace charge. The products of the blast furnace are:

• Lead metal	
• Matte	44-62% copper 10-20% lead 13% sulfur ∿2% zinc, iron and silica
• Speiss	55-65% copper, 8-18% lead, sulfur, arsenic, zinc, iron and silica
• Slag	Siliceous with 10-20% zinc ∿2% lead and ∿3% sulfur and some iron and sulfur

The fluorides contained in the sinter feed are not decomposed extensively in the sintering furnace or blast furnace. They are, however, decomposed at dross reverberatory furnace temperatures to a greater extent. The dross reverberatory furnace and refining kettles, which operate at gas temperatures from 1400° to 1800°F, constitute the lead refining process. The fluorides contained in the charge, would, based on thermochemical equilibria studies, be evolved quantitatively as gaseous HF at the upper temperature.

Figure 3-59 presents a process model and partial mass balance for a 271 ton (lead bullion) per day lead smelting plant.

Production Trends. Current (1967) production of lead bullion in the U.S. is 1.24 million tons. Assuming a 2% annual increase in production, lead bullion production in 2000 would be 2.4 million tons.


①
ORE AND LEAD CONCENTRATE
AIR AND NATURAL GAS
FLUX ③
SINTERING MACHINES 1200°F
②
ZINC PLANT RESIDUE
AIR
⑤
COKE
BLAST FURNACES 1000°-1200°F
④
⑥ SLAG
AIR
NATURAL GAS
LEAD REFINERY 1400°-1800°F
LEAD ⑦
COKE BREEZE
AIR
NATURAL GAS
DROSS REVERB 1600°-1800°F
MATTE AND SPERSS ⑧
RECYCLE
DUST COLLECTION
DUST COLLECTION
DUST COLLECTION
TO ATMOSPHERE OR SULFURIC ACID PLANT
⑨
TO ATMOSPHERE

Basis: Smelter capacity of 271 tons/day lead bullion
process streams - tons/24 hour day

Material	Stream Number								
	1	2	3	4	5	6	7	8	9*
HF									0.049
CaF_2	9.096								
Total Fluorides	0.096								0.049
Total as F	0.047								0.047
Pb	269	2		4		4	271	0.8	
Cu								1.8	
As								0.2	
Sb								0.1	
Fe								0.4	
Slag				128		161			
Other	91	46						0.7	
Flux			60						
Coke					66				
Offgas									72,000$^{(A)}$
Approx. Stream Total	360	48	60	132	66	165	271	4	–

Soluble flouride emission factor = 0.34 lb/ton lead produced
(A) SCFM at 32°F, 1 atm

Figure 3-59. Lead Smelting - Uncontrolled Process$^{(4271)}$

Fluoride Emissions. As with copper, the total lack of data in the literature made it necessary to estimate "average" fluoride content of concentrate charge to American lead smelters, fluoride evolved in the kettles and dross "reverbs," and overall fluoride emission factors. The average lead mineral (Pb, Zn and S) content of lead ore was estimated at 80%. The remaining 20% of the concentrates is assumed to be gangue minerals, with a fluoride content of 650 parts per million. Based on these assumptions and the others noted above, soluble fluoride emissions are estimated at 210 tons for 1967, and projected to be 408 tons in 2000 if current lack of control continues.

Fluoride Emission Control Techniques. There are no fluoride emission control techniques currently in use in the U.S.

3.13.4 Zinc Smelting and Refining Industry

The major primary ores of zinc are associated with a wide and varying range of fluoride containing minerals. As noted with copper and lead, the fluoride containing minerals vary widely in distribution through the ore body. The normal concentration steps employed for production of zinc concentrate do not separate the zinc sulfide ore completely from the other minerals. Detailed analyses of the various ores and concentrates produced in the U.S. are needed and are not available in the literature.

Industry Description. The primary zinc minerals are sphalerite (ZnS - 67% Zn), hemimorphite ($2\ ZnO \cdot H_2O \cdot SiO_2$ - 54.2% Zn) and smithsonite ($ZnCO_3$ - 52.1% Zn). Other minerals such as willemite, zincite and franklinite form a separate group found at Franklin Furnace, New Jersey. Neither lead nor zinc deposits have been found in immediate association with igneous rocks; they reach their places of precipitation in solution. The fluoride-bearing gangue minerals associated with the zinc bearing ore bodies are listed in Table 3-107.

Concentration of as-mined ore follows a typical sequence of crushing, gravity concentration, grinding and flotation. Assays of zinc concentrate (mainly from flotation systems) cluster in the fifties, with the majority below 55% Zn.

Zinc smelting follows an extraction process of roasting, sintering and calcining. Some plants both roast and sinter zinc sulfide concentrates before extraction. Calcining is performed only on oxide ores or on material that has previously been oxidized by roasting.

Zinc sulfide concentrates are usually converted by a roasting process to zinc oxide by any one of a number of types of roasters which typically remove 93 to 97% of the sulfur at temperatures that range between 1200° and 1900°F. At the higher temperatures, much of the fluorides present are driven off as gaseous HF. The Table 3-108 shows the temperature ranges of typical zinc roasting operations.

Table 3-108. Typical Zinc Roasting Operations (4271)

Type of Roaster	Operating Temperature, °F
Multihearth	1,200-1,350
Multihearth (2)	1,600-1,650
Ropp(3)	1,200
Fluid bed(4) (Dorr-Oliver)	1,640
Fluid bed(2) (Dorr-Oliver)	1,650
Fluid bed (Lurgi)	1,700
Suspension	1,800
Fluid column	1,900

(1)Dead roast except where noted otherwise.

(2)First stage is a partial roast in multihearth, second stage is a dry-feed dead roast in Dorr-Oliver fluid bed

(3)Partial roast

(4)Slurry feed

Sintering is used mainly to agglomerate a roaster calcine for subsequent processing. Operating temperature is typically 1900°F. Feed for the sintering operation is a mixture of calcine or concentrates, recycled ground sinter, and the required amount of carbonaceous fuel of proper particle size and moisture content for pelletizing. Those fluorides not volatilized in the roasting furnace are at least partially evolved in the sintering machine.

Calcining is a heat-treating process that is used for oxidized materials such as oxide ore concentrates or material from roasting of sulfide ore concentrates. It may be called nodulizing, since hard nodules of random sizes are produced when the calcining is done in a rotary kiln. The nodulized kiln product is subsequently treated for zinc extraction.

Roasting, sintering, and calcining are preliminary steps to one of the extraction methods: pyroreduction or leaching and electrolysis.

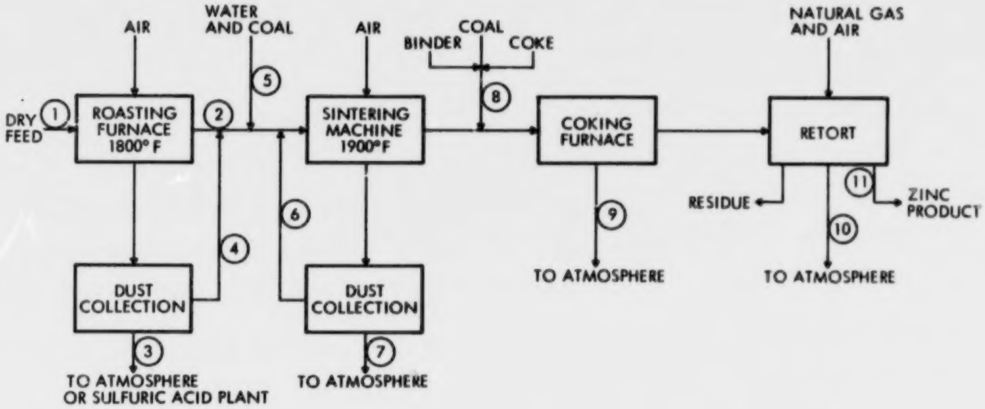
Pyroreduction distillation or retorting of the sinter or calcine is performed in horizontal or vertical retorts, electrothermal open or submerged arc furnaces, or blast furnaces. Horizontal retorts are small ceramic cylinders that are mounted horizontally in racks that hold several rows of retorts mounted one over the other. They are fed with coal and sinter and produce liquid zinc metal as do the larger and more modern vertical retorts.

Figure 3-60 presents the process model and mass balances for a 423 ton per day (zinc metal basis) smelter.

Production Trends. In 1968, primary slab zinc plants were operated in 14 locations with a capacity of 1.3 million tons and a production of 1.07 million tons. At the 2.5% rate of increase estimated for zinc production, U.S. zinc production in 2000 would be 2.4 million tons.

Fluoride Emissions. The procedure employed to develop estimates of fluoride emission for zinc smelting and refining is similar to those used for copper and lead production-associated fluoride emissions. The average zinc mineral content of zinc ore concentrates was estimated at 88%. The remaining 12% gangue minerals were assumed to have a fluoride content of 650 parts per million. On the bases of these assumptions and the others noted above, soluble fluoride emissions are estimated at 246 tons per year for 1967, and projected to be 550 tons per year in 2000.

Fluoride Emission Control Techniques. There are no fluoride emission control techniques currently employed in the industry.


AIR
WATER AND COAL
AIR
COAL
BINDER
COKE
NATURAL GAS AND AIR
DRY FEED
①
ROASTING FURNACE 1800° F
②
⑤
SINTERING MACHINE 1900°F
⑧
COKING FURNACE
RETORT
RESIDUE
⑪
ZINC PRODUCT
④
⑥
⑨
⑩
DUST COLLECTION
DUST COLLECTION
TO ATMOSPHERE
TO ATMOSPHERE
③
⑦
TO ATMOSPHERE OR SULFURIC ACID PLANT
TO ATMOSPHERE

Basis: Smelter capacity of 423 tons/day of zinc metal
process streams - tons/24 hour day

Material	Stream Number										
	1	2	3*	4	5	6	7	8	9*	10	11
HF			0.065						0.037		
CaF_2	0.12				0.009			0.060			
Total Fluorides	0.12		0.065		0.009			0.060	0.037		
Total as F	0.062		0.062$^{(C)}$		0.005			0.030	0.035		
Zinc	432	432									423
Sulfur	230	9									
Other	58	96									
Coal					49			304			
Coke								122			
Binder								30			
SO_2			443								
Dust			0.8	72		53	0.6				
Water	1				61						
Air (B)			44,300$^{(A)}$				73,620$^{(A)}$		58,520$^{(A)}$	44,480$^{(A)}$	
Natural Gas											
Approx. Total Stream	721	537	–	72	110	53	–	456	–	–	423

Soluble F emission factor = 0.46 lb/ton of zinc produced
(A) SCFM at 32°F, 1 atm
(B) Air defined as nitrogen, oxygen and carbon dioxide
(C) Ultimate fate of HF in acid plant undetermined

Figure 3-60. Zinc Smelting - Uncontrolled Process$^{(4271)}$

Table 3-107. Gangue Minerals

Note: The 78 minerals listed, which vary from common to extremely rare, are found in association with various ore bodies containing copper, lead and zinc ores of significance. The content of individual minerals contained in ore bodies, as well as fluoride content of any individual mineral, varies widely from undetectably low levels to major contamination. There is a variation in mineral content associated with ore body geology, as well as the variation in mineral content association with differences in ore bodies and ore types. This list was taken from Orsino C. Smith, *Identification and Qualitative Chemical Analysis of Minerals*, D. Van Nostrand Company, New York City, New York 1946 (Reference 4272).

Common

Pyrochlore	$Na, Ca, Cb_2 O_6.F$
Topaz	$Al_2O_3 \cdot (OH,F) \cdot SiO_2$
Chondrodite	$4M_g O \cdot 2SiO_2 \cdot M_g (F,OH)_2$
Fluorapatite	$9CaO \cdot 3P_2O_5 \cdot CaF_2$
Apatite	$3Ca_3(PO_4)_2 \cdot Ca(F,Cl)_2$
Fluorite	CaF_2
Cryolite	$3NaF \cdot AlF_3$
Zunyite	$Al_2O_3 \cdot SiO_2 \cdot Al(OH,F,Cl)_3$
Lepidolite	$(K,Li)_2O \cdot Al_2O_3 \cdot 3SiO_2$ with F

Uncommon

Matlockite	PbF, CL
Bastnaesite	$(Ce,La,Di)F.CO_2$
Marignacite	Variety of Pyrochlore
Durangite	$NaF,AlAsO_4$
Parisite	$2(Ce,La,Di,Th) OF \cdot CaO \cdot 3CO_3$

Uncommon

Cordylite	Fluocarbonate of Ce Metals and Ba
Cardylite	$BaF_2 \cdot Ce_2O_3 \cdot CO_2$
Chalcolamprite	$Na_4(CaF)_2 Cb_2 SiO_9$
Triplite	$(Fe,Mn) FPO_4$ with Ca and M_g
Metajarlite	$NaSr_3Al_3F_{16}$
Magnesium - Orthrite	$7 [(Mg,Fe,Ca)O + (Fe,Al,Ce, Cb,La)_2O_3], 6SiO_2 \cdot H_2O + F$
Fersmannite	$8(Ca,Na_2)(O,F_2) 4TiO_2 \cdot 3SiO_2$
Svabite	$9 Ca O \cdot 3 (As_2O_5 \cdot P_2O_5) Ca(F \cdot OH)_2$
Fermorite	$(Ca,Si)O \cdot (P,As)_2 O5 \cdot Ca(OH,F)_2$

Table 3-107. Gangue Minerals (Continued)

Uncommon	
Yttrofluorite	$(Ca_3Y_2)F_6$
Metatriplite	$6\ MnO\cdot 3P_2O_5\cdot 2\ (Mn,Ca)F_2\cdot 4H_2O$
Montebrasite	$Al_2O_3\cdot P_2O_5\cdot 2Li(OH,F)$
Ephesite	$(Na,Ca,Li)_2Al_4\cdot Si_2O_{10}(O,OH,F)_2$
Norbergite	$3MgO\cdot SiO_2\cdot H_2O$ +F
Edenite	$8CaO\cdot 2Na_2O\cdot 18MgO\cdot 4Al_2O_3\cdot 26SiO_2\cdot H_2O\cdot 3F_2$
Meliphanite	$2CaO\cdot 2BeO\cdot 3SiO_2\cdot NaF$
Sellaite	M_gF_2
Herderite	$Ca(F,OH)_2\cdot CaO\cdot 2BeO\cdot P_2O_5$
Tilasite	$2CaO\cdot MgO\cdot As_2O_3\cdot MgF_2$
Reddingite	$4P_2O_5\cdot 3H_2O$ +F
Hamlinite	PO_4 of Al and Ba with H_2O and F
Quercyite	$6CaO\cdot 2P_2O_5\cdot 2CaO\cdot 2CO_3\cdot CaF_2$
Francolite	$10CaO\cdot 3P_2O_5\cdot CaF_2\cdot CO_2\cdot H_2O$
Lecroixite	$2(Na,F,OH)\cdot 2(Mn,Ca)O\cdot Al_2O_3\cdot P_2O_5\cdot H_2O$
Pachnolite	NaF, CaF_2, $AlF_3\cdot H_2O$

Uncommon	
Zinnwaldite	$K_2O\cdot Li_2O\cdot FeO\cdot F_2\cdot 2Al_2O_3\cdot 6SiO_2\cdot H_2O$
Thomsenolite	$NaF\cdot CaF_2\cdot AlF_3\cdot H_2O$
Ellestadite	CaO, SO_3, SiO_2, P_2O_5, CO_2, Cl, F
Manganapatite	$9(Ca,Mn)O\cdot 3P_2O_5\cdot Ca(OH,F)_2$
Magnophorite	Ca,Na,K,Mg,Fe,Ti, Mn,Si,Al,Ti,O, OH,F
Cuspidine	$3CaO\cdot CaF_2\cdot 2SiO_2$
Wagnerite	$Mg_3(PO_4)\cdot MgF_2$
Weberite	Na_2MgAlF_7
Villiaumite	NaF
Fluoborite	$6MgO\cdot B_2O_3\cdot 3(H_2O,F_2)$
Creedite	$CaO\cdot 2Al(F,OH)_3\cdot 2CaF_2\cdot SO_3\cdot 2H_2O$
Pachnolite	$NaF\cdot CaF_2\cdot AlF_3\cdot H_2O$
Zeophyllite	$3CaO\cdot CaF_2\cdot 3SiO_2\cdot H_2O$
Custerite	$3CaO\cdot CaF_2\cdot 2SiO_2\cdot H_2O$
Prosopite	$CaF_2\cdot 2Al_2(OH,F)_3$
Bulfonteinite	$CaSiO_2\cdot (OH,F)_4$

Table 3-107. Gangue Minerals (Continued)

Uncommon	
Jezekite	$CaO\cdot Al_2O_3\cdot 2(Na,Li)F\cdot P_2O_5\cdot 2(Na,Li)(OH)$
Leucophanite	$NaF\cdot CaO\cdot B_2O_3\cdot 2SiO_2$
Morinite	$3Al_2O_3\cdot 2Na_2O\cdot 4P_2O_5\cdot 6CaF_2\cdot 18H_2O$
Chiolite	$5NaF\cdot 3AlF_3$
Cryolithionite	$3NaF\cdot 3LiF\cdot 2AlF_3\cdot 2K_2O\cdot 10(Mg,Fe)O$
Silicomagnesiofluorite	$H_2Ca_4Mg_3Si_2O_7F_{10}$
Polylithionite	$(Na,K)_3Li_5Al_2Si_8O_{22}F_8$
Gearksutite	$CaF_2\cdot Al(F,OH)_3\cdot H_2O$
Kurskite	$2Ca_3(PO_4)_2\cdot CaF_2\cdot CaCO_3$
Nocerite	$2\ MgO\cdot MgF_2\cdot CaF_2$
Hieratite	$2KF\cdot SiF_4$

Uncommon	
Cryophyllite	$3(Li,K)_2O\cdot 2FeO\cdot 4Al_2O_3\cdot 20SiO_2\cdot 3\ H_2O\cdot 8(Li,K)F$
Malladrite	$2\ NaF\cdot SiF_4$
Leifite	$Na_2O\cdot Al_2O_3\cdot 9SiO_2\cdot 2NaF$
Ralstonite	$(Mg,Na_2)F_2\cdot 3Al(F,OH)_3\cdot 2H_2O$
Sulphohalite	$2Na_2SO_4\cdot 2NaCl\cdot NaF$
Schairerite	$Na_2SO_4\cdot Na(F,Cl)$
Minyulite	$2K(OH,F)\cdot 2Al_2O_3\cdot 2P_2O_5\cdot 7H_2O$
Ferruccite	$NaBF_4$
Avogadrite	KBF_4 + 10% $CsBF_4$
Fluellite	$AlF_3\cdot H_2O$
Cryptohalite	$2NH_4F\cdot SiF_4$

3.14 OTHER INDUSTRIES

A number of miscellaneous processes which emit relatively small quantities of soluble fluorides are covered in this section. These are fluorine production, fluorocarbon chemical production, uranium fluoride production, aluminum anodyzing, and beryllium production. Because of the small quantities of fluorides emitted, no process control models, mass balances or economic analyses were developed.

3.14.1 Fluorine and Fluorocarbon Chemicals

General Discussion. Manufacturing processes for fluorine and derivative chemicals as noted earlier are different in two important respects from all other processes discussed in this report. First, the fluorine involved is a portion of both raw material and product. This creates an economic incentive to minimize fluoride losses. Second, the quantity and concentration of toxic fluorides constitute a potential hazard that requires special consideration to preclude adverse legal or regulatory action.

A literature survey indicates that the amount of fluoride emitted to the atmosphere from the fluorine and fluorocarbon manufacturing processes is very small.(4242,4244) Because of the highly toxic and corrosive nature of the feed or product materials (HF, F_2), extreme care is taken to control spills and leakage. Furthermore, gaseous effluent streams are generally scrubbed to remove all but trace quantities of fluoride compounds.

In fluorocarbon production, there are no gaseous effluent streams and all product streams are scrubbed to meet purity specifications. In these processes, the unreacted HF is removed as solid CaF_2 and disposed of in that form.(4242,4243)

Although definitive emission data have not been found, it is probable that the fluorine chemical industry does not present a significant fluoride emission problem, because of the high abatement efficiencies obtained by the use of the caustic scrubbers.

Figures 3-61 and 3-62 present flow diagrams for fluorocarbon production and for fluorine production, with control systems included as integral process elements.

3.14.2 Uranium Fluoride Production

General Discussion. UF_4, a solid below 969°C at 1 atm, is formed by reacting UO_2 with an excess of HF at 550°C. The solid UF_4 is then reacted at 250°C with F_2 produced on site to form UF_6 (sublimation point 56°C at 1 atm) which is then fractionated from any residual HF and F_2.

Production and Fluoride Emissions. Virtually all the UF_4 and UF_6 produced in the U.S. is manufactured in one plant operated by the Allied Chemical Company, Metropolis, Ill., on the Ohio River. This plant, which resumed production in 1968 after a 3-year shutdown, has a capacity of 100,000 tons UF_6/yr.(714,4233) Annual HF production in the U.S. is approximately 300,000 tons, of which the fraction used in atomic energy is under 10% and decreasing, so that the maximum consumption at Metropolis is 30,000 tons HF/yr.(4233,4234)

Although no information was found that applied directly to the Metropolis plant, information was found on two UF_6 conversion plants which are now closed - the National Lead Company facility at Fernald, Ohio, on the Miami River, and the Union Carbide Corporation facility at Paducah, Kentucky, upstream from Metropolis, Ill. on the Ohio River.(714) The National Lead facility recovered 85% of its HF effluent as 70% hydrous solution, which it sold in bulk. Union Carbide claimed a 95% recovery as the 70% hydrous solution. National Lead tried scrubbing the remaining 15% with $Ca(OH)_2$ or KOH. The KF was sold and the CaF_2 was buried. The $Ca(OH)_2$ scrubbing proved to be less expensive.

Unprecipitated fluoride which passed through the Fernald scrubber was stored and released into the Miami River on a schedule such that the concentration in the river water never exceeded 0.8 ppm.(714) For the first 10 months of 1955, the plant discharge into the river averaged of 16.1 tons F^-/month, which extrapolates to 194 tons F^-/year. Assuming that the Fernald and Paducah plants shared the production equally and that

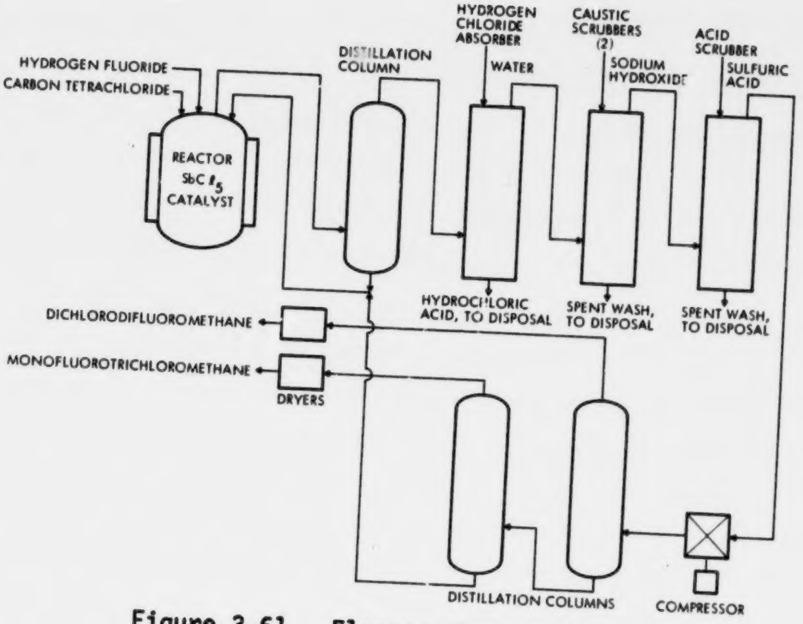

HYDROGEN CHLORIDE ABSORBER
CAUSTIC SCRUBBERS (2)
ACID SCRUBBER
DISTILLATION COLUMN
HYDROGEN FLUORIDE
CARBON TETRACHLORIDE
WATER
SODIUM HYDROXIDE
SULFURIC ACID
REACTOR
$SbCl_5$
CATALYST
HYDROCHLORIC ACID, TO DISPOSAL
SPENT WASH, TO DISPOSAL
SPENT WASH, TO DISPOSAL
DICHLORODIFLUOROMETHANE
MONOFLUOROTRICHLOROMETHANE
DRYERS
DISTILLATION COLUMNS
COMPRESSOR

Figure 3-61. Fluorocarbon Production

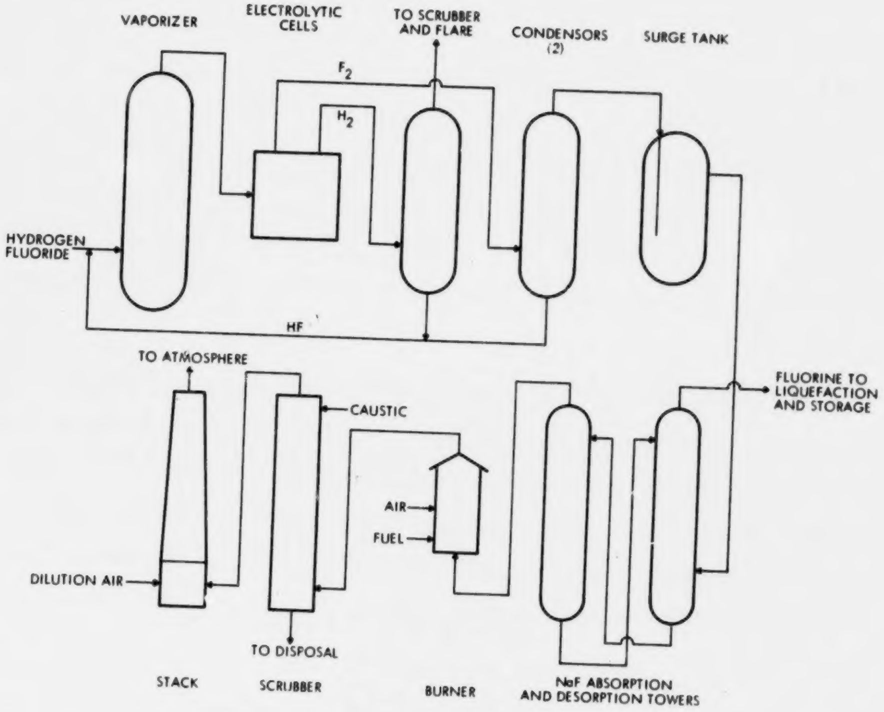

VAPORIZER
ELECTROLYTIC CELLS
TO SCRUBBER AND FLARE
CONDENSORS (2)
SURGE TANK
F_2
H_2
HYDROGEN FLUORIDE
HF
TO ATMOSPHERE
CAUSTIC
FLUORINE TO LIQUEFACTION AND STORAGE
AIR
FUEL
DILUTION AIR
TO DISPOSAL
STACK
SCRUBBER
BURNER
NaF ABSORPTION AND DESORPTION TOWERS

Figure 3-62. Fluorine Production

the Metropolis plant now operates under the same conditions, it is currently dumping approximately 400 tons F^-/year into the Ohio River if it is as efficient as the Fernald plant or 133 tons F^-/year if it is as efficient at the Paducah plant.

Furthermore, the Fernald plant buried 2500 tons HF/yr as CaF_2,(714) which would translate to 5000 tons/year for the Metropolis plant operating at the same recovery rate. Assuming a 99% efficiency for the $Ca(OH)_2$ scrubber, the 1% being vented through the stack amounts to 55 tons HF/year. For a 99.5% scrubber efficiency, 27 tons HF/year is being vented. If the Metropolis plant operates with the recovery rate of the Paducah plant, the atmospheric emissions are 18 tons HF/year and 9 tons HF/year for scrubber efficiencies of 99% and 99.5%, respectively.

3.14.3 Aluminum Anodizing

General Discussion. Mixtures of HF and HNO_3 are used in one process for cleaning Al alloys prior to anodizing or conversion coating with phosphate or chromate. The pretreatment typically consists of dipping batches of parts in a tank of solution containing 50 to 75% HNO_3 and 2 to 20% HF for 1 to 5 minutes at room temperature. If the Al alloy is particularly high in Si, a 3:1 HNO_3:HF solution might be used for 30 to 60 seconds at room temperature.(4237)

Dragout of the acid is considered economically undesirable for two reasons: (1) it wastes acid, and (2) it ruins the subsequent solutions and the final product. For this reason, all parts are carefully rinsed with cold water, and the wash is recycled to the acid bath. Baths are used over and over again until flocculation becomes excessive.(4236,4237)

For conversion coating, baths containing only 0.6% F ion are used. Again, as with cleaning baths, they are used over and over again.(4236,4237)

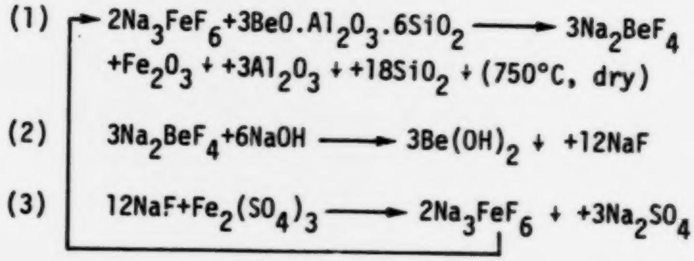
Production and Fluoride Emissions. The anodizing industry is very fragmented and consists of many small job shops, 58 of which are in the Los Angeles area alone. A spot telephone check of five shops chosen at random, showed an average consumption of 0.285 ton HF/year/plant with a maximum 1.27 tons.(4236) The largest user employed an alkaline scrubber mounted on the fume hood; the others had no controls for atmospheric emission. Since the Los Angeles Air Pollution Control District is one of the strongest pollution control agencies in the country, it may be assumed that these represent the most stringent control conditions.

An extrapolation on a population basis indicates that the total national use of HF in the anodizing industry amounts to 668 tons per year. The worst possible case from a pollution standpoint would be total volatilization as HF and uncontrolled venting of the HF. This would correspond to an annual national evolution of 668 tons HF (635 tons as soluble fluorides) by 2320 plants, or an average 0.29 ton HF/year/plant.

3.14.4 Beryllium Production

General Discussion. There are two beryllium producers in the U.S., Brush Beryllium and Kawecki-Berylco (formerly the Beryllium Corporation of America). The production is in three stages: (1) the naturally occurring beryl ($BeO.Al_2O_3.6SiO_2$) is converted to $Be(OH)_2$, (2) the $Be(OH)_2$ is converted to BeF_2, and (3) the BeF_2 is reduced to Be metal. The total annual production is 90 tons (as Be metal).(4154)

There are two processes currently in use for the production of $Be(OH)_2$ — the fluoride process used by Kawecki-Berylco and the sulfate extraction process used by Brush Beryllium.(4154) Only the fluoride process involves fluoride and consequent fluoride emissions. The reactions are:



(1) $2Na_3FeF_6 + 3BeO.Al_2O_3.6SiO_2 \longrightarrow 3Na_2BeF_4 + Fe_2O_3\downarrow + 3Al_2O_3\downarrow + 18SiO_2\downarrow$ (750°C, dry)

(2) $3Na_2BeF_4 + 6NaOH \longrightarrow 3Be(OH)_2\downarrow + 12NaF$

(3) $12NaF + Fe_2(SO_4)_3 \longrightarrow 2Na_3FeF_6\downarrow + 3Na_2SO_4$

The sodium fluoferrate is largely recovered and recycled. Some is lost, however, by volatilization as FeF_3, AlF_3 and SiF_4 in reaction (1), by entrainment in the discarded precipitated oxides resulting from the leaching of the products of reaction (1) with water, by entrainment with the $Be(OH)_2$ precipitate of reaction (2), and by solution in the discarded Na_2SO_4 filtrate of reaction (3). If an overall 80% recovery efficiency is assumed for the Na_3FeF_6, and if $Be(OH)_2$ production by the fluoride process accounts for half the total, the maximum amount of fluoride released by uncontrolled emission to the atmosphere, in precipitates and in effluent streams would amount to 93 tons per year as soluble F.

The $Be(OH)_2$ obtained by the fluoride process is further treated by dissolving in sulfuric acid, adding organic chelating agents such as the Na salt of ethylene diamine tetraacetic acid (EDTA), and neutralizing with NH_4OH to reprecipitate a highly purified $Be(OH)_2$. The $Be(OH)_2$ filter cake containing 50% free water is reacted with 35% excess NH_4HF_2 to yield BeF_2 after dehydration on a drum dryer. The 35% excess fluoride is volatilized.(4154) If this volatilization is uncontrolled, the maximum total atmospheric emission is 74 tons/year as soluble fluoride

The BeF_2 is converted to Be metal by reduction with Mg.(4154) By this stage, the toxicity of the materials because of their Be content far overshadows the fluoride problem, so that adequate effluent control is provided.

The maximum fluoride emission that can be expected, therefore, from the beryllium industry is 167 tons per year as F, assuming 20% of the Na_3FeF_6 input is lost to recovery and recycling and the volatilization of the ammonium fluoride species in the BeF_2 production is uncontrolled.

4. RESEARCH AND DEVELOPMENT PLANNING

4.1 SUMMARY AND PRIORITIES

Section 3 discussed industrial sources of fluoride emissions to the atmosphere. In many of the industries discussed, definitive information related to emission levels is not available, i.e., input fluoride concentrations, output quantities, release mechanisms, etc. Research and development (R&D) projects have been planned and prioritized which will expand the informational base and provide the knowledge and methodology required to improve fluoride emission control.

Table 4-1 presents a summary of the recommended projects by industry and objective. Table 4-2 presents the relative priority and time phasing of each project together with the approximate rate of expenditure required to fund all programs. Table 4-3 summarizes the manpower, cost, and calendar time requirements of the programs in the same format as Table 4-1.

An examination of Table 4-1 shows projects which are primarily oriented toward collecting information on fluoride inputs, and improving the level of understanding of the process mechanisms releasing and collecting fluorides. The single exception is development of control processes for the ion and steel industry. This emphasis resulted from the current lack of information of this type for the indicated industries. Once the process characteristics are known, existing control device technology will probably be applicable. The recommended projects have been planned in reasonable detail and are presented in the following section. Additional R&D work will be required for each industry, based on the results obtained from the recommended projects, to apply the knowledge gained to development and economic evaluation of applicable control processes. Since the specifics of the additional work will be determined by the results of the recommended projects, detailed plans have not been formulated. It is anticipated that in each case a project will be required that is roughly similar in approach, resources, and time to that recommended for development of control processes for the iron and steel industry.

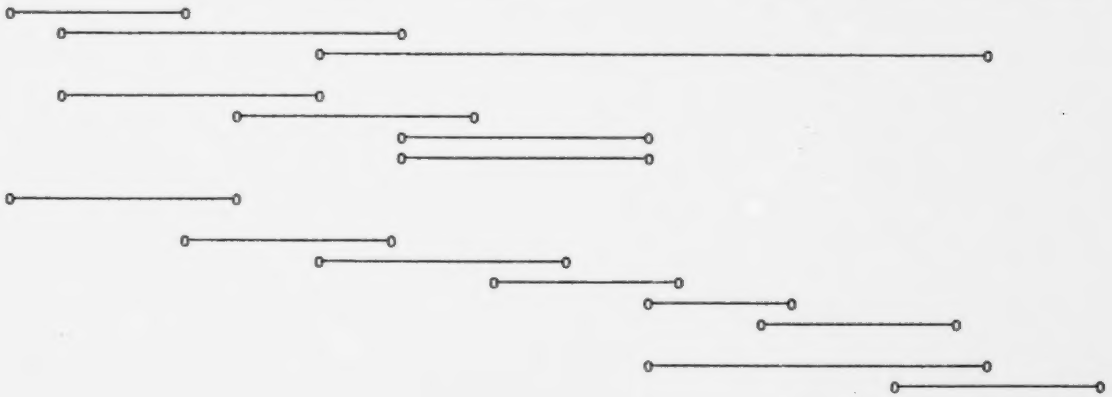
The prioritization shown in Table 4-2 is based on the quanitity of soluble fluorides emitted from a particular industry, both current and projected, and the state of knowledge of fluoride emission in the industry.

Table 4-1. Fluoride Emission Control - Recommended Research and Development Projects by Industry

Project Type Industry	Feed/Ore Fluoride Content Characterization	Determination of Fate of F in Mfg. Process	Determination of Fate of Fluoride Evolved	Development of F Control Techniques	Determination of Fate of F in Control Process
Aluminum			1) Experimentally determine F capture by hoods and define building control requirements and characteristics		
Iron and Steel	1) Experimentally determine and verify average F contents of iron ore bodies and sinter/pellet plant charges for U.S. regional areas	2) Experimentally determine species and quantities of F cpds evolved and emitted by primary iron/steel production processes		3) Design, develop and test on bench and portable pilot plant economic, effective F emission control processes for iron/steel	
Coal Burning Steam-Electric Power	1) Experimentally determine by U.S. regional area F, alkali, and alkaline earth metal contents and variabilities of coal	2) Experimentally determine the F species emitted by coal combustion as function of feed composition 4) Experimentally determine effect of S&N purification processes on fluorides in coal and effect of fluorides on processes			3) Experimentally determine quantities and types of F cpds removed by current and projected SO_2 control processes and effect on processes
Cement, Ceramic and Glass	1) Experimentally determine by U.S. regional areas the F contents of cement feedstocks 3) Experimentally determine the F content of feedstocks and process streams in frit mfr. 4) Experimentally determine by U.S. regional areas the F content of heavy clay product and expanded clay aggreg. feedstocks	2) Experimentally determine F species and quantities emitted in cement mfr. as function of feedstock F content 5) Experimentally determine F species and quantities emitted in heavy and expanded clay products mfr. as function of feed			
Non-ferrous metals	1) Experimentally determine the F contents of Cu Pb Zn ores and feedstocks by geographical area	2) Experimentally determine F species and quantities evolved and emitted in Cu Pb Zn smelting as functions of feed and process parameters			3) Experimentally determine the F species and quantities emitted from smelter by-product H_2SO_4 plants as functions of process parameters and feeds

Table 4-2. Fluoride Emission Control - Recommended Research and Development Priority and Time Sequence

Industry	Project No.	Priority
Iron & Steel	1	1
	2	2
	3	3
Coal	1	4
	2	5
	3	6
	4	7
Aluminum	1	8
Cement Ceramic & Glass	4	9
	5	10
	3	11
	1	12
	2	13
Non-Ferrous Metal	1	14
	2	15



	YEAR NO. 1				YEAR NO. 2				YEAR NO. 3				YEAR NO. 4	
	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II
Approx. Expenditure Per Quarter $M	48	96	94	92	153	151	148	133	123	132	116	130	23	15

Table 4-3. Fluoride Emission Control - Recommended Research and Development Types and Costs by Industry

PROJECT INDUSTRY	ORE FLUORIDE CONTENT CHARACTERIZATION	DETERMINATION OF FATE OF F IN MFG. PROCESS	DETERMINATION OF FATE OF FLUORIDE EVOLVED	DEVELOPMENT OF F CONTROL TECHNIQUES	DETERMINATION OF FATE OF FIN CONTROL PROCESS
Aluminum			Prof. Man Hrs. - 1720 Non-Prof. Man Hrs. - 1620 Total Cost - $70,000 Time Span - 9 Months (1)		
Iron & Steel	Prof. Man Hrs. - 1200 Non-Prof. Man Hrs. - 1500 Total Cost - $60,000 Time Span - 7 Months (1)	Prof. Man Hrs. - 1600 Non-Prof. Man Hrs. - 2000 Total Cost - $85,000 Time Span - 12 Months (2)		Prof. Man Hrs. - 12400 Non-Prof. Man Hrs. - 12000 Total Cost $580,000 Time Span - 24 Months (3)	
Coal Burning Steam - Electric Power	Prof. Man Hrs. - 1360 Non-Prof. Man Hrs. - 2410 Total Cost - $75,000 Time Span - 9 Months (1)	Prof. Man Hrs. - 1160 Non-Prof. Man Hrs. - 1680 Total Cost - $62,000 Time Span - 8 Months (2)			Prof. Man Hrs. - 1750 Non-Prof. Man Hrs. - 1330 Total Cost - $65,000 Time Span - 9 Months (3)
		Prof. Man Hrs. - 1400 Non-Prof. Man Hrs. - 1080 Total Cost - $55,000 Time Span - 9 Months (4)			
Cement, Ceramic & Glass	Prof. Man Hrs. - 760 Non-Prof. Man Hrs. - 900 Total Cost - $45,000 Time Span - 6 Months (1)	Prof. Man Hrs. - 870 Non-Prof. Man Hrs. - 1030 Total Cost - $48,000 Time Span - 7 Months (2)			
	Prof. Man Hrs. - 880 Non-Prof. Man Hrs. - 1040 Total Cost - $48,000 Time Span - 7 Months (3)	Prof. Man Hrs. - 1080 Non-Prof. Man Hrs. - 1080 Total Cost - $61,000 Time Span - 8 Months (5)			
	Prof. Man Hrs. - 1000 Non-Prof. Man Hrs. - 1240 Total Cost - $53,000 Time Span - 7 Months (4)				
Non-Ferrous Metals	Prof. Man Hrs. - 1700 Non Prof. Man Hrs. - 2500 Total Cost - $93,000 Time Span - 12 Months (1)	Prof. Man Hrs - 1200 Non- Prof. Man Hrs. - 600 Total Cost - $61,000 Time Span - 8 Months (2)			Prof. Man Hrs. - 1200 Non-Prof. Man Hrs. - 1200 Total Cost - $64,000 Time Span - 9 Months (3)

4.2 DETAILED PROJECTS BY INDUSTRY

The following R&D projects are recommended.

4.2.1 Primary Aluminum Smelting Industry

Project 1. Determination of the Fluoride Capture Efficiency of Pot-Line Hoods

Introduction

Primary aluminum production is both a present and a projected major source for soluble fluorides emitted to the atmosphere. Virtually all of the soluble fluorides emitted by the industry come from the reduction process pot-lines. Total emissions of soluble fluorides during 1970 for the industry are estimated at 16,200 tons. Over 70% of this total is estimated to be accounted for by fluoride evolution which escapes capture by the pot-line hood system.

In view of the quantity of soluble fluorides involved, hood capture efficiency must be known accurately. The current estimates of hood capture efficiency are based upon industry responses to an OAP sponsored questionnaire. Direct experimental verification of the industry-provided values is required.

Objectives

1. Determination of the effectiveness and efficiencies under normal and "sick-pot" operating conditions of each of the different types of pot-line hoods.
2. Definition of the requirements for and characteristics of pot-line building effluent capture and abatement devices.

Approach

1. Based on statistically designed experiments and sampling plans, experimentally determine the amount of fluorine-containing materials captured by the fume collecting devices for each of the three basic smelter types, under normal and (insofar as possible) "sick-pot" operating conditions.

2. Experimentally determine the effect that different types of fume collecting equipment and different collection techniques have on the effectiveness of collection of the fluoride effluents from the pots.
3. Determine experimentally the efficiency of the building fume collection hoods and the conditions under which they operate.
4. Estimate, from experimental data derived around operating smelters, the actual overall efficiencies of the fume collection devices.
5. Define the operating characteristics for building collection systems and abatement devices.

Tasks

1. Design a statistically based experiment to obtain the required information on the fume capture efficiencies of the hoods used with the three pot types.
2. Experimentally determine by flow measurement, sampling and analyses the quantity of fluorine compounds (fluorides) collected by the pot-line fume collection devices for each of the three basic smelter types for a 1 day period.
3. Experimentally determine by flow measurement, sampling and analyses the quantity of fluorides emitted through the pot-line building ventilation devices.
4. Determine experimentally the effects of variations in individual pot fume collection devices on fluoride capture efficiency as per (2) and (3) above.
5. Estimate, the actual efficiency of the pot fume collection hoods, when in operation, either singly or manifolded.
6. Estimate the overall pot-line fume collection efficiencies for each smelter type.
7. Define the flow characteristics for pot-line building ventilation systems, to provide allowable building fluoride concentration levels, and capture of fluorides which escape the pot hoods.
8. Define the characteristics of building effluents that abatement systems will be required to handle in terms of flow, gaseous and particulate fluoride concentrations, other contaminant concentrations, gas composition, temperature, and pressure.

Costs

Professional Man-Hours	1,720
Nonprofessional Man-Hours	1,620
Computer Units	4
Other Direct Costs	$5,000
Total Cost	$70,000
Time Span	9 Months

4.2.2. Iron and Steel Manufacture

Introduction

The manufacture of iron and steel produced an estimated 64,600 tons of soluble fluoride emissions in 1968, and, if current practices continue, will produce 46,400 tons of soluble fluoride emissions in 2000. Almost all of the emissions occur in ecologically sensitive urban areas. Relatively little has been reported in the open literature on the fluoride content of the iron ores employed in this country. With the exception of scanty reports on the emission of soluble fluorides associated with the use of high fluoride ore at one plant location, almost no data exist on the fate of the fluorides fed into the various iron and steel production processes as contaminants and fluxes. Finally, only one control process has been employed, at one plant location only, for the specific purpose of controlling fluoride emissions.

The highest priorities have been assigned to research and development projects designed to eliminate the lack of factual experimental data resulting from the above deficiencies. The three projects are: (1) quantitative determination of fluoride contents of iron ores by geographical area, (2) determination of the fate of fluorine compounds in the current iron and steel industry, and (3) development of a cost-effective fluoride control technique utilizing current state-of-the-art techniques.

The research and development plans presented in the following discussion cover the above three projects, which are designed to operate with a considerable degree of parallelism, thereby significantly diminishing the potential elapsed time required. Descriptions of the individual projects together with schedule, level of effort and cost estimates are presented.

Project 1. Determination of Fluoride Content of Iron Ores by Geographical Area

The main purpose of this project is to determine the quantities of fluorides present in the different iron ores used in the United States. Very little data now exist on the total amount of fluorine present in the iron ores from the various domestic and foreign sources used in current iron and steel manufacturing operations. The determination of fluoride concentrations is necessary for planning operations over the next several years, for abatement and also for process development.

Objectives

1. Determine the fluoride content of the iron ore used as raw material for the production of iron and steel in each of the major industry areas in the United States.
2. Determine the average fluoride content of iron ore representative of each of the major ore bodies employed as raw material sources.

Approach

1. Utilizing statistical experimental design techniques, determine the quantity of iron ore samples from each given location and the number of locations required to provide valid estimates of the mean fluoride content and its variance.
2. Collect iron ore samples from the various active mines supplying the iron and steel industry in each of the selected areas.
3. Collect iron ore samples from feed to the ore sintering plants in each of the selected areas.
4. Utilizing accepted quantitative analytical chemical techniques, determine the fluoride concentrations in the ore samples. This is to include an investigation of the various fluoride analytical techniques, selection of the best methods and experimental design of the testing procedure to provide valid statistical information.
5. Map the United States into regional areas with respect to mean fluoride distribution for both sinter plant raw material feed and ore body source.

6. Verify the above raw material fluoride content values by using the blending ratios employed as the bases for calculating plant feed fluoride content from ore body fluoride concentrations.

Tasks

1. Design a statistically based experiment to yield the number of samples required from each location.
2. Design a statistically based experiment to give the number of locations to be sampled to provide the desired information.
3. Collect the number and type of samples required from each location.
4. Perform an evaluation of the analytical methods to be used in the project.
5. Analyze the samples collected as per Task 3.
6. Obtain the blending ratio employed at the plant locations sampled.
7. Reduce the analytical data to provide the appropriate statistics.
8. Map the various statistical data to provide the functions of geographical distribution required.
9. Cross check the sinter-plant* feed analytical values by comparison with those derived from blending ratios and ore-source fluoride analyses.

Costs

Professional Man-Hours	1,200
Nonprofessional Man-Hours	1,500
Computer Units	8
Other Direct Costs	$4,000
Total Cost	$60,000
Time Span	7 Months

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*For the purposes of this project sinter plant and pelletizing plants are synonymous.

Project 2. Determination of the Fate of Fluoride Compounds in the Iron and Steel Industry

The main purpose of this project is to determine experimentally the species and quantities of fluoride compounds evolved and emitted by the primary iron and steel production processes. The data will be used to verify the values estimated by use of thermochemical analysis, and will serve as one basis for selection of control processes. The primary iron and steel production processes to be investigated include iron ore sintering and pelletizing operations.

Ojectives

1. Determination of the quantity, type and distribution of fluoride compounds evolved during the primary iron and steel production processes.
2. Determination of the quantity and form of the fluoride species emitted from iron and steel operations.

Approach

1. Utilizing statistical experimental design techniques, determine the sampling plan required to provide valid experimental data on the fluoride species and mean fluoride compound concentration levels in the iron and steel fabricating process feed streams, product streams, by-product streams and stack effluents.
2. Examine the various sampling and analytical chemical techniques and select the best methods of analysis.
3. Utilizing the selected sampling and analytical chemical techniques, determine the fluoride and cofactor values of the process streams and effluents.
4. Incorporate the above information into a correlation model which can be utilized to predict both fluoride amounts and fluoride species found in the process effluent streams as a function of the input ore composition and process fluoride additives.
5. Utilizing the correlation model in 4 above, tabulate the fluoride amounts and species for the process effluent streams.

Tasks

1. Design the statistically based sampling plan required to obtain valid experimental data on the fluoride species and individual fluoride compound concentrations in the feed streams, product streams, and other process effluents for each of the four basic iron and steel producing processes (iron ore sintering and pelletizing, and blast and open hearth furnace operations).
2. Evaluate the various available sampling and chemical analytical methods, and select those to be used in the project.
3. Collect the numbers and types of samples required by the sampling techniques selected.
4. Determine the fluoride species and fluoride and cofactor values for each of the process streams by the chemical analytical methods selected.
5. Utilize the above information to synthesize a correlation model for prediction of fluoride species evolution and emission as functions of ore and flux fluoride charge quantities.
6. Tabulate the fluoride emission values appropriate to the various ores, additives and process conditions in common use.

Costs

Professional Man-Hours	1,600
Nonprofessional Man-Hours	2,000
Computer Units	16
Other Direct Costs	$8,000
Total Cost	$85,000
Time Span	12 Months

Project 3. Development of Cost Effective Fluoride Control Techniques

The main purpose of this project is to develop, through fundamental studies, engineering evaluations and pilot plant studies, a cost effective fluoride control technique for each of four primary iron and steel production processes. Only one (very expensive) fluoride control facility is now in operation and a more cost effective system is necessary, especially where there are low concentrations of fluoride compounds in the process effluents. The control of soluble fluorine compound emissions represents a major abatement process development effort in the iron and steel industry. Utilizing the approach specified below, cost effective techniques can be developed for the control of soluble fluoride emissions in the iron and steel industry.

Objectives

1. Determine the specific applicability of current fluoride control techniques (both wet and dry) to iron and steel operations.
2. Determine the fluoride control costs as a function of equipment, plant size and efficiency.
3. Provide new, more economical (compared to the U.S. Steel processes) control through current control process modifications.

Approach

1. Through a literature search and direct contact with equipment manufacturers, verify prior findings on the materials of construction, capital costs and operating costs of processes and equipment potentially suitable for fluoride control in the iron and steel industry.
2. Perform detailed parametric analyses (utilizing computer simulation) of the pollutant control economics with input fluoride concentration, species and control efficiency as the variable parameters.
3. Perform engineering studies on theoretically modified current control techniques for removal of fluorides from the effluents of the iron and steel industry. Evaluate the effects these changes may have on process economics and efficiencies.
4. Under laboratory conditions simulate the most effective modification made to control processes and verify the effect on fluoride emission of these changes.
5. Evaluate the most promising processes on a pilot plant scale at representative iron and steel processing facilities.
6. Provide detailed recommendations of economically optimal fluoride pollutant control systems for various plant sizes and configurations.

Tasks

1. Perform a literature search to verify materials of construction, capital costs and operating costs of processes and equipment potentially suitable for fluorine control in the iron and steel industry.
2. Initiate direct contact with equipment manufacturers to verify prior findings on the materials of construction, capital costs and operating costs of processes and equipment potentially suitable for fluorine control in the iron and steel industry.
3. Prepare a mathematical model to simulate pollution control economics.
4. Perform parametric analyses (utilizing computer simulation) of the pollution control economics with input fluoride concentration, species and control efficiency as the variable parameters.
5. Perform engineering studies on theoretically modified control techniques for removal of fluorides from the iron and steel effluents.
6. Evaluate the effects the changes to the basic processes have on the economics and efficiencies of the iron and steel operations.
7. Simulate under laboratory conditions the most effective modifications to control processes.
8. Utilizing laboratory scale mini-plants, verify the effect modifications to control processes have on fluoride emissions.
9. Construct a portable pilot plant of the most promising process.
10. Operate the portable pilot plant at representative iron and steel facilities.
11. Evaluate the analytical results of the pilot plant testing.
12. Provide detailed recommendations of economically optimal fluoride pollutant control systems for various plant sizes and configurations.

Cost

Professional Man-Hours	12,000
Nonprofessional Man-Hours	12,000
Computer Units	40
Other Direct Costs	20
Capital Equipment Cost	50
Total Cost	$580,000
Time Span	24 Months

4.2.3 Coal Combustion

Introduction

The combustion of coal represents a major probable source of hydrogen fluoride emission and, therefore, requires considerable emphasis on the investigation and development of techniques for the abatement of pollution from this source. The specific deficiencies identified in the course of the Fluoride Emissions Control Study will be eliminated by: (1) quantitative statistical assessment of the means and variances of the fluoride content of coals from the various actively mined beds; (2) experimental determination of the fate of the fluorine in the combustion, heat transfer and various effluent streams of coal-fired systems; (3) determination of the effect of various control processes designed to remove sulfur dioxide from flue gases on the types and quantities of fluoride produced as well as the effects of fluoride contamination on these processes and ultimate by-products recovery; and (4) determination of the effects of the various coal pretreatment processes on fluoride content in the final fuel form and the effect of the fluorides on these processes and ultimate recovery.

The research and development plans presented in the following discussion consist of four projects, each addressed to solve a specific deficiency, designed to operate with a considerable degree of parallelism thereby significantly diminishing the potential elapsed time required. Descriptions of the individual projects together with time requirements, level of effort and cost estimates are presented below.

Project 1. Determination of the Fluoride Content of Coal

The quantities and types of fluoride containing pollutants emitted by coal-fired combustion systems depend first on the quantity of fluorine contained in the coal and, second, on the types and quantities of other elements whose combustion products might react with or adsorb fluorine compounds. Since the limitation of fluoride emissions might require restrictions on the quantity of fluoride contained in the coal and since the forms in which the fluoride is evolved could effect the design of potential abatement processes, a determination is required of the averages and variances associated with the content of fluorine, alkali and alkaline earth metals, and possible adsorbents.

Objectives

1. To determine the species and expected weight percent ranges for the fluoride, alkali and alkaline earth metals and possible adsorbents in coal.
2. To determine the geographical distribution of the fluoride and other specific components in coal.

Approach

1. Utilizing statistical experimental design techniques, determine the quantity of coal samples from a given location and the number of locations required to provide valid estimates of the mean fluoride content and its variance. Since the vast majority of coal consumed for power plant usage comes from the area of the U. S. east of the Mississippi River, the Eastern Interior and Appalachian Regions, initial efforts should be concentrated in this area. Typical major producing beds of interest are: the Pittsburgh, Upper and Lower Kitanning, Freeport and the Illinois No. 5 and 6 which correspond to neighboring areas in Indiana and Western Kentucky. Obtain required coal cofactors (heat values, ash content and metals content) from literature/suppliers.
2. Collect coal samples from the various active mines in the selected areas which supply power plants.
3. Utilizing qualitative and quantititive chemical analytical techniques, determine the fluoride and other specified species concentrations. This is to include an investigation of the various available analytical techniques, selection of the best techniques, and experimental design of the testing procedures to provide valid statistical information.
4. Map the major U. S. regional areas with respect to mean fluoride and other specified element distributions.

Tasks

1. Determine from historical information available from the Bureau of Mines the variability of ash content, sulfur concentration, and other factors and use these data to assess the number of samples required to provide accurate statistics.
2. Perform a literature survey to identify candidate techniques for the determination of the various elements of interest.
3. Based on Bureau of Mines and ASTM coal sampling techniques and other information derived from 1 and 2 above, determine the types, sizes and sources of samples to be taken from the various coal beds.
4. Test the various chemical analytical techniques for accuracy, sensitivity and reproducibility; select the best procedures, and develop new methods where necessary.
5. Collect the indicated number, type, and size samples from the selected sources.
6. Perform the appropriate analyses on the samples.
7. Reduce the analytical data to provide the appropriate statistics.
8. Map the various statistics as a function of geographical distribution.

Costs

Professional Man-Hours	1,360
Nonprofessional Man-Hours	2,410
Computer Units	8
Other Direct Costs	$4,000
Total Cost	$74,000
Time Span	9 Months

Project 2. Determination of the Fate of Fluorides in the Power Plant Combustion Process

Direct experimental data on the fate of the fluoride compounds in the coal burned in steam-electric power plants is essential to proper design of abatement processes, and for corroboration of the high priority currently assigned to this source because of the estimated present and future magnitude of soluble fluoride emissions. These are, for 1970, an annual emission rate of 27,000 tons of HF; for 2000, a projected emission rate of 86,000 tons of HF.

Objectives

1. Determination of the quantity, form and distribution of fluoride species in the products of coal combustion in the power plant environment.

2. Determination of the effect of other coal composition factors, e.g., quantity and types of metals, ash content, etc., on the fluoride distribution.

3. Development of a quantitative chemical model of a typical power plant for predicting the fate of fluorides in the combustion products as a function of input coal types.

Approach

1. Utilizing statistical experimental design techniques, determine the sampling plan required to provide valid estimates of the mean fluoride compound concentration levels in power plant feed streams, ash residues, purification solutions and stack effluents.

2. Utilizing qualitative and quantitative analytical chemical techniques, determine the fluoride and cofactor values of the various power plant streams. This is to include in-depth analysis of the various analytical techniques and the selection of the best techniques.

3. Incorporate information into a correlation model which will be utilized to predict both fluoride amounts and species found in the power plant effluent streams as a function of the input coal composition.

Tasks

1. Design a statistically based experiment to determine the sampling plan for feed streams, ash residues, purification solutions and stack effluents to provide valid estimates of the mean fluoride concentration levels.

2. Perform a literature survey to determine the best possible analytical procedures for fluorine compounds.

3. Evaluate the available qualitative and quantitative chemical analytical methods.

4. Utilizing the coal composition information obtained in Project 1, a thermodynamic equilibrium program and a kinetic rate program, determine the probable chemical products formed and the quantities expected from the combustion of coal.

5. Sample representative power plant streams as per the sampling plan.

6. Analyze the samples by the selected methods for fluoride species and concentrations.

7. Perform a statistical evaluation of the data.

8. Design a correlation model utilizing the above information, to predict both the fluoride levels and species to be found in the power plant effluent streams as a function of input coal composition.

Costs

Professional Man-Hours	1,160
Nonprofessional Man-Hours	1,680
Computer Units	10
Other Direct Costs	\$4,000
Total Cost	\$62,000
Time Span	8 Months

Project 3. Concurrent Removal of SO_2 and Fluoride Combustion Products from Power Plant Stack Gas

Several processes have been proposed for the removal of sulfur dioxide (SO_2) from coal burning power plant stack gas. An evaluation of the effect of these processes on the fluoride compounds in the stack gas, and of the fluoride compounds on the scrubbing process chemistry and equipment is desirable to allow design of units which will remove detrimental fluoride compounds from the stack gas concurrently with the SO_2, and to insure that the fluoride compounds will not adversely effect the SO_2 scrubbing process chemistry or cause premature equipment failure.

Objectives

1. Determination of the quantities and types of fluoride compounds (evolved from combustion of coal and present in power plant stack gas) removed in selected current and projected SO_2 scrubbing processes.

2. Determination of the chemical products formed by the reacted and/or absorbed fluoride, and the effects of these fluorides on process equipment in terms of corrosion, scaling, etc.

3. Determination of the changes in the scrubbing system product/by-product make resulting from the fluoride compound uptake.

Approach

1. Utilizing the correlation model developed in Project 2, determine the fluoride compound product distribution expected in coal-fired power plant flue gas.
2. Utilizing existing literature data, estimate the effect of expected fluoride compounds on current and projected catalytic SO_2 removal processes.
3. Utilizing existing literature data, estimate the effect of expected fluoride compounds on wet scrubbing process chemistry.
4. Utilizing existing literature data, estimate the effect of expected fluoride compound reaction products on process equipment, both in terms of scaling and corrosion.
5. Conduct a market study to determine the impact of fluoride reaction product inclusion in SO_2 pollution abatement process by-products.
6. Propose a laboratory or pilot plant experimentation study designed to enhance available data to allow a full assessment of the SO_2/fluoride concurrent removal process design problems.

Tasks

1. Making use of the data already collected in Project 1, organize the input data available on fluoride concentrations and compounds existing in several typical boiler fuel coals.
2. Utilizing the correlation model developed in Project 2, determine the probable chemical products formed from combustion of the several typical boiler fuel coals.
3. Identify the current and projected most promising flue gas SO_2 abatement processes.
4. Conduct a literature search, and determine the effects of the expected fluoride compounds on current and projected catalytic SO_2 abatement processes.
5. Identify the current and projected most promising wet scrubbing processes for SO_2 removal from flue gas.

6. Utilizing literature information, determine the effect of the expected fluoride reaction products on the wet scrubbing chemistry, including potential side reactions.

7. Determine the scaling, erosion, and corrosion potential of fluoride compounds removed by and formed in the wet scrubbing circuit utilizing literature data and information.

8. Utilizing the information generated in Tasks 4 and 6, above, conduct a user-oriented market survey to determine the effect of fluoride content in potentially salable products from SO_2 pollution abatement process.

9. Identify the gaps in knowledge required to completely assess the effect of SO_2 abatement processes on fluoride emissions and of fluoride content of stack gas or SO_2 abatement processes.

10. Propose an experimental program to develop required data to satisfy gaps in the published data identified in Task 9, above.

Costs

Professional Man-Hours	1,600
Nonprofessional Man-Hours	1,300
Computer Units	6
Other Direct Costs	$1,000
Total Cost	$65,000
Time Span	9 Months

Project 4. Determine the Effect of Current and Projected Coal Purification (Sulfur Removal) on Captive Fluorides

The purpose of this project is to determine the effect of coal purification by the removal of sulfur compounds on the fluoride compound levels of the coal. The reactions of the fluorine species in the coal to the different solvent systems, to organic sulfur compounds removal and to inorganic sulfur compound removal processes will be investigated. Since sulfur removal from coal is in its infancy, the main emphasis of the fluoride program will be to determine potential process impact.

Objectives

1. Determination of the portion of the captive fluorides in the various coals removed by chemical reaction or leaching during the treatment (both current and projected processes) of coal for sulfur removal.

2. Determination of the form of the reacted fluorides and their impact on process equipment and by-products.

Approach

1. Determine the probable reaction products and confirm the probable product distribution expected under process reaction conditions.

2. Utilizing statistical experimental design techniques, undertake a laboratory study to confirm the theoretical results.

3. Knowing the form of the fluoride reaction products, estimate their effects (corrosiveness and material compatibility) on current and projected process equipment design.

4. Through a market study, determine what impact the fluoride reaction products will have on the marketability of by-products (mainly sulfur compounds).

Tasks

1. Utilizing thermodynamic equilibrium and kinetic rate data, determine the fluoride compound product distribution expected under different process reaction condition, i.e., residence time, temperature and pressure.

2. Using statistical experiment techniques, design a laboratory study to validate the theoretical results.

3. Conduct a literature search and determine the effects of the expected fluoride compounds on current and projected sulfur removal processes.

4. Identify the current and projected most promising sulfur removal processes.

5. Utilizing the literature information, determine the effect of the expected fluoride reaction products on the sulfur removal chemistry, including side reactions.

6. Conduct a laboratory scale verification to confirm theoretical compounds.

7. Estimate the effects of the fluorine compounds on process design for the sulfur removal process.

8. Perform a literature search on the effect the fluoride compounds will have on materials of construction and on potential corrosion of process equipment for the current and projected desulfurization processes.

9. Conduct a user-oriented market survey to determine the effect of fluoride content on potentially soluble products from desulfurization of coal.

Costs

Professional Man-Hours	1,340
Nonprofessional Man-Hours	1,000
Computer Units	8
Other Direct Costs	$500
Total Cost	$55,000
Time Span	9 Months

4.2.4 Cement, Ceramic and Glass Manufacture

The cement, ceramic and glass industries (glass manufacture, frit smelting, heavy clay product, expanded clay aggregate, and cement) involve high temperature production of vitreous or refractory shapes from siliceous raw materials. In all of the industries, fluorides are a part of the raw material charge - either accidentally, as contaminants, or deliberately, as additions.

There is almost no data available on the fluoride content of the raw material charges, or on the fluoride species and quantities evolved and emitted. It is estimated, however, on the basis of the sparse information available, that these "silicate" industries currently emit 19,300 tons of soluble fluorides per year, and will emit 42,200 tons per year by 2000. Knowledge of the fluoride content of the feed materials, and the fluorides evolved, is mandatory for adequate control design. As a first step toward this goal, research and development programs are proposed in the following sections to assess the amounts of fluorine compounds in various feedstocks and to determine their fate in the actual production processes.

Project 1. Determination of Fluoride Concentrations in Production Feedstocks by Geographical Areas

As a prerequisite to accurate definition of the problem of fluoride pollution, and to adequate design of an appropriate control program, the exact chemical nature and quantity of the pollutants must be determined. For cement production, the fluoride emission originates from the feedstock components which contain fluorine compounds. Hence, it is pertinent to know the quantity of fluorides present in the various feedstocks to the cement production process.

Objectives

1. Determination of the fluorine content of the various feedstocks to the cement production process.
2. Establishment of the geographical distribution of the various feedstocks with respect to their total fluoride contents.

Approach

1. Based on statistical principles for the design of experiments, develop a sampling plan which will produce valid and representative estimates of the mean fluorine content and its variance at each chosen geographical area.
2. Collect the samples according to the sampling plan from the various sources supplying cement plants in the selected areas.
3. Utilizing the best qualitative and quantitative chemical analysis techniques, determine the concentrations of fluorine in the samples.
4. Relate the mean fluorine content of each cement feedstock component to the U.S. regional area where it originates. This will establish the geographical distribution of fluorine-containing feedstock components in the U.S.

Tasks

1. Utilizing statistical techniques for experimental design, set up a sampling plan which determines the size and number of the samples from a given location, and the number of locations required from each geographical area.
2. Collect the required samples according to the plan determined in Task 1.
3. Assess the various available methods for quantitative chemical analysis for fluorine and select the best method for the feedstocks. Modify the existing methods or develop a new method if necessary.
4. Perform the chemical analyses required for the samples taken.
5. Reduce the analytical data obtained in Task 4 to yield the desired statistics.
6. Map the various statistics as a function of geographical distribution.

Cost

Professional Man-Hours	760
Nonprofessional Man-Hours	900
Computer Units	4
Other Diurect Costs	$10,000
Total Cost	$46,000
Time Span	6 Months

Project 2. Determination of Fluorides Emitted by the Cement Production Processes.

Before any work can be planned and undertaken to develop an economically feasible process to control or reduce the fluoride emission from the cement production process, it is necessary to know the chemical identities and quantities of the fluorine compounds evolved and emitted. This research and development program is proposed to obtain the needed information.

Objectives

1. Identify and determine the quantities of all fluorine compounds emitted by the cement production processes.
2. Develop a correlation model to relate the emitted fluoride species and their amounts to the feedstock fluoride content.

Approach

1. Based on statistical methods for experimental design, develop a sampling plan to provide valid estimates of the mean fluorine compound concentration levels in the feed streams and the stack effluent streams for cement production plants.
2. Evaluate the available sampling, qualitative and quantitative analytical methods to determine the best methods to obtain and analyze the samples taken.
3. Sample and perform the analyses.
4. Use the analytical data to develop a mathematical correlation which can be utilized to predict both the fluoride species and their amounts in the effluent streams as a function of the feedstock fluoride content.
5. Apply the correlation to obtain the fluorine species and contents of stack effluents from cement plants.

Tasks

1. Utilizing statistical methods for the design of experiments, establish a sampling plan which will determine the size and number of samples to be taken at each given location and the number of locations required from each geographical area.

2. Evaluate the various available methods for sampling and qualitative and quantitative chemical analysis for fluorine. Select the best methods for the various streams. Make any modifications necessary or develop a completely new method if necessary.

3. Collect the required samples according to the above sampling plan and methods.

4. Perform the chemical analyses for all samples taken.

5. Use the test results to develop a mathematical correlation relating the types of fluorine compounds and quantities discharged in the effluent streams to the feedstock component composition.

6. Utilize the correlation developed in Task 5 to compute the fluorine contents of the stack effluents for the various fluoride ranges found in Project 1.

Costs

Professional Man-Hours	870
Nonprofessional Man-Hours	1030
Computer Units	8
Other Direct Costs	$5,000
Total Cost	$48,000
Time Span	7 Months

Project 3. Determination of Fluorides in the Effluents of Opal Glass and Enamel Frit Production Processes

Fluorine compounds such as fluorspar, cryolite, etc. are among the many components used in opal glass and enamel frit productions. As a result, some 3,300 tons of hazardous fluorides are emitted from these sources every year. In order to develop the technology needed to reduce the fluoride emissions from these industries, it is necessary to determine the species and quantities of the fluorine compounds present in the effluent streams under normal operation conditions, and how are they effected by minor variations in the feed compositions. It is the purpose of this proposed project to obtain the needed information.

Objectives

1. Identify and determine the quantities of all fluorine compounds found in the effluent and production streams of the opal glass and enamel frit production processes.

2. Determine the effect of variations in the fluoride content of the feed components on the fluoride content and distribution in the effluent and production streams.

3. Develop a mathematical model to relate the fluorides input in the feed to the fluorides in the effluent streams.

Approach

1. Based on statistical principles, establish a sampling plan for taking samples from the feed streams, the product streams, and the effluent streams from opal glass and enamel frit production processes.

2. Utilizing the best techniques for qualitative and quantitative chemical analysis, determine the fluorine content of various process streams.

3. Correlate the experimental data to form mathematical models which will be utilized to perdict the fluoride species and quantities in the effluent streams as a function of the input fluoride.

4. Apply the mathematical models to compute the stack effluent fluoride concentration level for each fluoride species.

Tasks

1. Utilizing statistical methods for designing experiments, set up a sampling plan which specifies the optimum size and number of samples to be taken from a given location and the number of locations for each geographical area.

2. Collect the samples according to the sampling plan of Task 1.

3. Investigate various techniques for qualitative and quantitative chemical analysis for fluorine compounds. Select the best analytical method. Develop a completely new method if necessary.

4. Perform the chemical analyses on all samples taken. (Note: Feed stream samples are to be analyzed quantitatively only for fluoride content. No qualitative analyses need be performed on feed streams.)

5. Analyze and correlate the test data to yield correlation models which may be used to predict the fluoride species and amounts in the effluent streams from the fluoride contents of the feed.

6. Utilize the correlation models developed in Task 5 to compute the stack effluent concentrations for each fluoride species for the various fluoride ranges found for the feed streams.

Cost

Professional Man-Hours	880
Nonprofessional Man-Hours	1040
Computer Units	8
Other Direct Cost	$4,000
Total Cost	$48,000
Time Span	7 Months

Project 4. Determination of Fluoride Concentrations of Clay Product Feedstocks from Various Geographical Areas

Heavy clay products and expanded clay aggregates contribute an estimated 15,000 tons per year of soluble fluorides to current atmospheric pollution. To verify this estimate, and to enable proper control planning, knowledge of the fluoride contents of the various production feedstocks is required.

Objectives

1. To determine the fluorine content of the various feedstocks to the heavy clay and expanded clay aggregate plants.

2. To establish the geographical distribution of the various feedstocks with respect to their total fluoride contents.

Approach

1. Compile all available data on chemical compositions of feedstocks for clay products from various geographical locations.

2. Based on statistical principles, set up the sampling and experimental plan to characterize the feedstocks.

3. Collect samples from various geographical areas.

4. Utilizing best available chemical analysis techniques, determine the fluoride contents of all samples taken.

5. Map the variations in the fluoride content of the feedstocks as a function of geographical areas.

Tasks

1. From a literature search and other available sources, compile data on chemical composition of feedstocks used for producing various clay products. It is necessary to have data covering a wide range of geographical areas.
2. Utilizing a statistical method for experimental design, establish a sampling plan which specifies the optimum size and number of samples to be taken from a given location and the number of locations required.
3. Collect the samples according to the plan set up in Task 2.
4. Investigate various techniques for chemical analysis of fluorine. Select the best analytical method. Develop a completely new method if necessary.
5. Perform the chemical analyses of all samples taken.
6. Correlate the results of chemical analyses and the literature data with the locations of samples to establish the fluorine content in the feedstocks as a function of the geographical areas.

Cost

Professional Man-Hours	1,000
Nonprofessional Man-Hours	1,240
Computer Units	6
Other Direct Costs	$5,000
Total Cost	$53,000
Time Span	7 Months

Project 5. Determination of Fluorides Emitted by the Heavy Clay and Expanded Clay Aggregate Processes

Accurate knowledge of the fluoride species and quantities evolved and emitted by the heavy clay and expanded clay aggregate production processes as functions of the feedstock fluoride contents is required for optimum design of control processes. This project is designed to obtain that knowledge experimentally over a wide range of feedstocks and plants.

Objectives

1. To identify and determine the quantities of all fluorides emitted by the heavy clay and expanded clay aggregate processes.

2. To develop correlation models to relate the emitted fluoride species and their amounts to the feedstock fluoride content.

Approach

1. Based on statistical methods for experimental design, develop a sampling plan to provide valid estimates of the mean fluorine compound concentration levels in the feed streams and the stack effluent streams for heavy clay and expanded clay aggregate production plants.
2. Evaluate the available sampling and qualitative and quantitative analytical methods to determine the best methods to be used to obtain and analyze the samples taken.
3. Sample and perform the analyses.
4. Use the analytical data to develop mathematical correlations which can be utilized to predict both the fluoride species and their amounts in the effluent streams as a function of the feedstock fluoride content.
5. Apply the correlations to obtain the fluorine species and contents of stack effluents from heavy clay product and expanded clay aggregate plants.

Tasks

1. Utilizing statistical methods for the design of experiments, establish a sampling plan which will determine the size and number of samples to be taken at each given location and the number of locations required from each geographical area.
2. Evaluate the various available methods for sampling, and qualitative and quantitative chemical analysis for fluorine. Select the best methods for the various streams. Make any modifications necessary or develop a completely new method if necessary.
3. Collect the required samples according to the sampling plan and methods selected.
4. Perform the chemical analyses for all samples taken.
5. Use the test results to develop a mathematical correlation relating the types of fluorine compounds and the quantities emitted in the effluent streams to the feedstock fluoride content, for each process.

6. Utilize the correlations developed in Task 5 to compute the fluorine contents of the stack effluents for the various fluoride ranges found in Project 4.

Costs

Professional Man-Hours	1080
Nonprofessional Man-Hours	1080
Computer Units	18
Other Direct Costs	\$4,500
Total Cost	\$61,000
Time Span	8 Months

4.2.5 Nonferrous Metals Smelting and Refining Industry

Copper, lead and zinc sulfide ores are smelted and refined to yield the three nonferrous metals, and an unknown amount of soluble fluoride emission. The nonferrous metals industry is a potentially major source of soluble fluoride compounds. Little is known or available on the fluoride contents of the various sulfide ores. Considerable sampling and analytical effort will have to be expended to provide description of the potential problem with sufficient adequacy and accuracy for the definition of control requirements and processes. The various methods and processes used to concentrate and smelt the ores, and to refine the metals will have to be investigated, in conjunction with investigation of by-product recovery processes, to determine experimentally the effects of the process steps and parameters on fluoride emission.

Project 1. Determination of Fluoride Content of Copper, Lead and Zinc Ores by Geographical Location

At the present time very little is known about the fluoride content of the various copper, lead and zinc ores. This investigation will characterize by geographical location and ore type the amounts of fluorine present. This information, used as data base for a thermochemical equilibrium program, will yield a reasonable approximation of the types and quantities of fluorides that can potentially be liberated in the ore smelting and refining processes.

Objectives

1. Determination of the mean fluoride concentrations and variability of fluoride content in feedstock ores.
2. Determination of the effect of geographical location on the distribution of fluoride content within common feedstocks.

Approach

1. Locate and identify current mining areas in the U.S.
2. Develop statistically valid experimental sampling plans and quantitative analytical approaches for determining mean concentrations and variability of fluoride content of concentrates as a function of geographical locations and concentration processes.
3. Collect ore and concentrate samples.
4. Utilizing the selected quantitative chemical analysis techniques, determine the required fluoride information.
5. Map U.S. regional areas with respect to fluoride distributions.
6. Summarize the effects of identified concentrating processes on ore fluoride content.
7. Determine the effect of process parameters in concentrating methods on fluoride content.

Tasks

1. Perform a literature search to identify and locate current copper, lead and zinc ore mining areas in the U.S.
2. Perform a literature search to identify and locate the current copper, lead and zinc smelting and refining areas in the U.S.
3. Design a statistically based experiment for the determination of the average fluoride content of the various ores and concentrates, and for the determination of the variabilities of the fluoride content.
4. Experimentally develop quantitative analytical approaches and procedures for the determination of the fluoride contents of the ores and concentrates.

5. Collect samples from all geographical locations where mining and smelting operations are being conducted.

6. Experimentally determine the required analytical data on the samples collected in (5) above.

7. Prepare a map of the United States showing by areas, the different fluoride distributions based upon "as mined" and "concentrate" fluoride levels and variabilities.

8. Analyze the different processes for concentrating ores and summarize the effects of each step on the fluoride content of the processed material.

9. Identify and point out the impact of process parameters, including equipment, on the change in concentration of fluoride containing materials in the process.

Costs

Professional Man-Hours	1,700
Nonprofessional Man-Hours	2,500
Computer Units	4
Other Direct Costs	$10,000
Total Costs	$86,000
Time Span	12 Months

Project 2. Determination of the Fates of the Fluorides in the Nonferrous Metal Smelters and Refineries

In each of the sulfide ore smelting and refining processes, the species and quantities of fluorides evolved and emitted will be determined, as functions of feed ore fluoride concentrations and production process parameters. This information is not available in either private or open literature. The project will provide this information, to an extent sufficient for emission control process planning and design.

Objectives

1. Determine the chemical species and quantities of the fluorides evolved and emitted by the nonferrous metal smelting and refining processes.

2. Determine valid functional relationships between fluoride content of feed ores, process parameters and evolved and emitted fluorides

3. Develop correlation models of the smelting processes, to relate the evolved and emitted fluoride species and quantities to fluoride ore feed content and process parameters.

Approach

1. Utilizing statistical experimental design techniques, determine the sampling plan required to characterize the process stream fluoride levels and process parameters for each of the smelter types and each of the metals.
2. Select appropriate sampling and chemical analytical techniques for the determination of fluoride species and concentrations in the various process streams.
3. Use the selected sampling plan and sampling and analytical techniques to obtain and analyze the various process stream samples.
4. Incorporate ore analytical process and mass balance information into correlation models for predicting fluoride effluents as functions of ore fluoride content and process parameters.

Tasks

1. Design the statistically based sampling plans required to characterize the process parameters and process stream fluoride species and fluoride levels for each smelter type and each metal.
2. Select appropriate sampling and fluoride identification and determination procedures.
3. Collect the samples and analyze them for fluoride species and content, as per the plans and procedures selected.
4. Develop correlation models to predict fluoride species and quantities evolved and emitted as functions of ore fluoride content and process parameters.

Costs

Professional Man-Hours	1,200
Nonprofessional Man-Hours	600
Computer Units	16
Other Direct Cost	$10,000
Total Cost	$61,000
Time Span	8 Months

Project 3. Determination of Fluoride Compound Fate During By-Product Sulfuric Acid Production Processes

Many nonferrous metal sulfide ore smelters have an associated sulfuric acid plant, to utilize the by-product sulfur dioxide formed in the smelting process. The main purpose of this program is to determine the fate of the fluorine compounds evolved and emitted in the smelting processes.

Objective

1. Determination of the extent of fluoride compound removal during the by-product sulfuric acid production process.

Approach

1. Identify current sulfur dioxide emission control processes associated with the smelting of copper lead and zinc sulfide ores.
2. Develop and execute statistically valid experimental plans to sample the fluoride collection efficiencies and product and effluent fluoride contents characteristic of the processes.
3. Determine the effect of different ores, different processes and process parameter variations on fluoride collection characteristics and fluoride emissions.

Tasks

1. Perform a literature search to identify the current nonferrous metal smelter sulfur dioxide control processes.
2. Design a statistical sampling plan to determine the fate of smelter emitted fluoride in the processes.
3. Perform sampling operations as per Task (2) each of the selected processes.
4. Select appropriate qualitative and quantitative analytical techniques.
5. Analyze collected samples as per the techniques selected.

6. Develop correlation models to predict the fluoride species emitted from the by-product sulfuric acid plants, as functions of metal species, ore fluoride content, smelter process parameters, and sulfuric acid plant process parameters.

Costs

Professional Man-Hours	1,200
Nonprofessional Man-Hours	1,200
Computer Units	10
Other Direct Cost	$8,000
Total Cost	$64,000
Time Span	9 Months

5. ENVIRONMENTAL EFFECTS

The effects of fluorides are discussed in terms of the lowest concentration, less than one part per billion (ppb), that causes detectable changes in vegetation and then the effects of increasingly higher concentrations of gaseous fluorides are outlined. Included are: tip-burn observed on the leaves of sensitive vegetation, other agricultural effects, etching of glass, effects on man and some effects of process streams on building structures.

5.1 VEGETATION EFFECTS

Claims of damage from fluorides are usually related to biologic effects, and many studies have been performed. Five recent literature reviews have been published on fluoride effects.(4355,4158,4356,4159,4357) The largest single listing of published reports related to the biological effects of fluorides is an annotated fluoride bibliography.(4358)

McCune(4355) lists four types of fluoride effects on vegetation considered important in developing air quality criteria for fluorides: (a) visible effects such as necrosis (injured portions of leaves die and become discolored, also called tip-burn), (b) a diminution in the growth or in the yield of fruit or seeds caused by fluoride injury, (c) changes in physiological activities, metabolic activities and cellular structure with or without visible injury, and (d) deposit and accumulation of fluoride in the plant with increasingly higher fluoride concentrations in its tissues.

The lowest concentration of hydrogen fluoride (HF) reported to cause damage was 0.5 ppb when gladiolus plants were exposed continuously for 12 days. The leaf damage was well below the 10% of the leaf area considered necessary to cause damage in terms of either growth or yield. Thus, no economic loss would be attributed to this minimum detectable fluoride effect.

Examples of exposures that do relate to leaf damage and potential crop reduction are shown in Table 5-1. The spread of concentrations and exposure durations is quite broad: from 0.7 ppb for a period of 15 days for sorghum to 700 ppb over a period of 10 days for alfalfa. Other data state the lower limits for visible damage to citrus trees, other fruit trees, and certain evergreen trees (conifers); but for these plants, the data are not yet adequate to predict reduction in crop values.(4355) Additional data presented for alfalfa show the relationship between levels of HF exposure and the fluoride accumulated in the plant leaves. These data are important considering the potential use of this crop as animal feed and will be discussed further in the next section.

The accumulation of fluoride in plant tissues can increase gradually and cause no injury to the plant even though the level of accumulated fluoride may have exceeded the level that is safe for ingestion by animals. Attempts to relate fluoride levels in plant tissues to injury, if any, to the plant tissues have not been useful. Fluoride levels in plant tissues alone can be misleading and have not been shown to be a dependable basis for judging injury to plants. Hence, they will not be considered further here.

Table 5-1. Examples of HF Concentrations (ppb) and Exposure Durations Reported to Cause Leaf Damage and Potential Reduction in Crop Values(4355)

Plant	Concentration and Time
Sorghum	0.7 ppb for 15 days (most sensitive varieties)--15 ppb for 3 days (most resistant varieties)
Corn	2 ppb for 10 days--800 ppb for 4 hours
Tomato	10 ppb for 100 days--700 ppb for 6 days
Alfalfa	100 ppb for 120 days--700 ppb for 10 days

A large collection of experimental data is available relating effects of gaseous fluorides to vegetation damage. Comparatively little information is available for relating particulate fluoride levels to vegetation damage. The most that can be said is that fluoride dusts are far less injurious to vegetation than are the gaseous fluorides.

Another aspect of fluoride effects on vegetation concerns exposures to dissolved fluorides. A fluoride solution such as sodium fluoride administered to plants receiving all nutrients by solution feeding through their roots has produced typical fluoride injury. Tip-burn from fluoride solutions resembles the damage seen in leaves exposed to HF in air. This suggests the possibility of damage to vegetation through fluoride contamination of the soil. This has not been observed in the field, probably because of the presence of sufficient calcium and aluminum in soils to inactivate the fluoride. Some fluoride can be absorbed from the soil but at relatively slow rates. Hence, reports of fluoride damage and related crop losses have been attributed to fluorides entering the plants from the air through their leaves.

The most susceptible plants show evidence of damage when exposed to HF concentrations in the range of 0.5 to 1.2 ppb provided there is continuous exposure for periods of several days. This group includes gladiolus, sorghum, conifers, corn, citrus trees and certain other fruit trees. Much higher levels of HF, 300 to 1000 ppb for periods of exposure as short as 7 hours, will damage a wide variety of plants. Data on very high levels of exposure are mostly limited to tests in experimental fumigation chambers.

5.2 EFFECTS ON FARM ANIMALS

Fluorides may accumulate on and in plant tissues and raise the fluoride level high enough to make that vegetation hazardous if eaten by farm animals. This is particularly important in connection with fluoride accumulations in pasture grass, hay crops, and silage since these foods are so widely fed to livestock. Fluoride levels in these materials at levels of 40-50 parts per million (ppm) on a dry weight basis may cause injury in some farm animals if consumed continuously over long periods of time (years) even though the accumulation of fluoride in the vegetation has induced no detectable plant damages. When there is reason to refer to fluoride absorbed by plants or deposited on the surfaces of the leaves, the fluoride units are usually 1000 times larger, parts per million, then the units used above for describing the exposures of plants to gaseous fluorides, parts per billion A unique group of plants in the tea family may accumulate quite high fluoride levels, 1000 to 2000 ppm, and show no evidence of fluoride damage. Since these plants are not used as food for farm animals, no agricultural problems have been reported; however, these fluoride levels have been given some attention in terms of the use of tea as a beverage. It should be noted that fluoride accumulates in leaves but appears in only negligible amounts in seeds or fruit produced by plants having high fluoride levels in the leaves.

The fluorides in industrial emissions inhaled by farm animals have not been observed to have an injurious effect; however, an important aspect of fluoride accumulation by vegetation arises from accumulation of fluoride dusts on leaves of plants and blades of pasture grass. The dusts may be noninjurious to the vegetation but contain hazardous amounts of fluoride in terms of forage for farm animals. Ingestion of fluoride has been investigated extensively in many species of animals including man. Phosphate rock is an example of a dust that seemingly has not injured plants but is injurious to farm animals. This was made evident in the 1930's when an attempt was made to use the calcium and phosphate in this mineral as a dietary supplement. Fluoride injury quickly became apparent. Other data on phosphate rock in relation to animal feeding are included below.

In overwhelming dosages fluorides cause toxic effects in several vital systems of animals. Vegetation containing well above 5000 ppm of fluoride would be needed to cause such effects in farms animals; and since these high levels are not observed in pastures and fields, acute effects will not be considered further.

Experimental feeding of cattle with feed containing fluorides at levels of 600-1200 ppm was started but interrupted after 18 days because of the rapidly diminished food intake. The fluoride was then administered separately from the food to maintain more uniform dosage levels. The experiments were terminated after about four months for the highest fluoride level and about six months for the lowest fluoride level. Loss of appetite caused food consumption to decrease more than 50%, and the outstanding effect was that of starvation.(4361) Since concentrations of fluoride in pasture grass as high as 2000 ppm were reported in 1946(4362) but are no longer being observed near industrial emission sources, these very high levels need not be considered further.

Levels of fluoride ingestion resulting from contamination of forage with industrial fluoride emissions are usually well below those noted above and acute fluoride effects are not likely to be found today. Considerable experimental data have been published describing the effects of ingesting foods containing 20-200 ppm of fluorides. Ingestion at these levels by farm animals causes fluoride effects primarily related to the site where fluorides accumulate to the greatest extent, the bones and teeth of the exposed animals. These effects, listed in order of appearance in exposed animals, are:

(a) Dental lesions (primarily damage to incisor teeth)
(b) Hyperostosis (overgrowth of the bones)
(c) Lameness
(d) Loss of appetite
(e) Decreased milk production
(f) Diminution in reproduction(4158,4356)

Items (e) and (f) result from loss of appetite caused by fluoride intake. This secondary effect makes (e) and (f) somewhat contraversial.

The dietary fluoride intake need only be at the level of 20 to 30 ppm in the food in order for detectable dental changes to develop among cattle. However, these earliest changes amount only to white spots in the enamel of the teeth and are not harmful. Continuous ingestion of food containing 40 to 50 ppm causes dental changes in cattle that are severe enough to cause the eventual destruction of the incisor teeth through excessive attrition. This leads to loss of ability to graze normally, a reduced intake of food and a series of problems that result in economic losses amoung herds exposed continuously to food containing levels of fluoride in the range of 40 to 50 ppm.

Generally, the ill effects of fluoride pollutants among exposed farm animals develop slowly. If forage levels do not exceed 50 ppm fluorides, exposures continuing 5 years or more may be required for the maximum economic losses to develop. As the fluoride levels are gradually increased, the time required for the ill effects to appear is progressively reduced.

Another factor governing the severity of the effects of fluoride ingestion is the age of the animals when fluoride exposure is started. If the animals are mature, all teeth will have erupted and no injury to the incisor teeth may be expected. Even so, excessive bone growth leading to lameness can still develop. Except for fluoride effects on bones and teeth, other potentially harmful effects caused by higher levels of fluoride, 100 ppm and above, are secondary to the effects related to loss of appetite and the resulting decreased food intake.

Not all types of fluorides deposited on forage are equally hazardous. Also, not all animal species are as susceptible as cattle to ingested fluorides. Both of these factors are shown in Table 5-2 in terms of related dosages and related toxicities.(4359)

Table 5-2. Safe Average Levels of Fluorides in the Total Ration of Farm Animals(4359)

	Fluoride Source	
Species	Soluble Fluoride Such As Sodium Fluoride (F, ppm)	Phosphate Rock or Phosphatic Limestone (F, ppm)
Dairy Cattle	30-50	60-100
Beef Cattle	40-50	65-100
Sheep	70-100	100-200
Chickens	150-300	300-400
Turkeys	300-400	no data

Very little information is available relating the concentrations of fluorides in industrial process emissions to the fluoride concentrations in pastures or alfalfa fields. Information about fluoride concentrations adjacent to sources of the fluoride emissions is frequently obtained through monitoring programs which involve periodic ambient air sampling and fluoride analysis of vegetation obtained from the pastures, fields, or orchards. However, corresponding information on source emission rates of fluorides and their relationships with the ambient concentrations have not been reported. Some experimental laboratory data exist that suggest that fluoride will accumulate above the safe levels for cattle if alfalfa is continuously exposed to a level of HF at 1 ppb for as long as 100 days.(4355) No similar data have been published relating ambient dust concentrations to levels of fluoride accumulated in or on forage. It is apparent that, in general, source emissions cannot currently be definitively related to environmental effects. The series of events including emission dispersion, fallout, chemical reaction, assimilation, and effect contains too many uncertainties to be accurately described.

Determination of the magnitude of fluoride ingestion by livestock can be accomplished by measurement of fluoride excreted in urine and for fluoride accumulated in sections of rib or tail bones (removed by biopsies). These quantities will increase in proportion to the levels of exposure of the animals.(4359) Neither type of measurement has been related directly to either ambient air fluoride levels or to rates of emissions of fluorides from industrial processes.

5.3 FLUORIDE EFFECTS IN MAN

Information describing the effects of fluorides in man has come from observations concerning both inhalation and ingestion of fluorides. Inhalation data were collected in connection with potential exposure of workers to atmospheric fluorides. Data related to ingestion of fluorides were obtained for several reasons, but the greatest amount of information came from investigations concerned with fluorides in drinking water supplies. Together, these data provide usable guidelines for judging fluoride effects such as: (a) levels of urinary fluoride excretion as a function of the level of exposure, (b) fluoride retention in the bones of exposed persons. (c) radiologic evidence of excessive fluoride deposition in bones. Changes in tooth enamel are also useful for judging exposure to fluorides; however, since this effect does not occur after the teeth erupt, its usefulness is limited to exposure occurring during childhood. Fluoride treatments given to reduce bone loss (osteoporosis) in some elderly patients have also provided useful information related to effects of fluoride in man. Data related to very large doses of fluoride have been obtained from cases of accidental poisoning or attempted suicide. These aspects of fluoride effects are included in the review by Hodge and Smith.(4159)

The teeth of children have shown fluoride effects related to the fluoride in their drinking water. These dental effects, which appear clearly when the water contains fluoride at the level of 2 ppm, are more pronounced at 3 ppm and are described as severe when 4 ppm is reached or exceeded. For persons whose teeth have erupted, no dental effects occur and no other skeletal or organic ill effects from these levels have been found in the United States. The effects of fluorides among children have been investigated in areas where the potential for industrial emissions of fluoride were believed to exist. Hodge and Smith (4159) cite two reports from Russia alleging dental effects among children. In contrast to this, a survey made among children residing near aluminum plants in Vancouver, Washington, and Ft. William, Scotland, revealed no effects attributable to exposure to fluorides.(4363,4364)

Because of a nearby aluminum plant, total atmospheric fluoride levels in and around Ft. William, Scotland, were measured and reported to range between 59 and 130 ppb. The gaseous fraction was reported to be 7 to 120 ppb.(4364) The investigation was made primarily to judge the fluoride effects among factory employees and farm animals; but other groups of residents were also surveyed. A group of adults consisting of 26 men and 51 women not employed at the factory were given clinical examination, and all but two of that group were also given X-ray examinations. A group of 113 children were also given the same examinations. No significant fluoride effects were observed among these residents. Dental changes among a few of the children were not considered to be solely the result of fluorides in the air since the past history of these children could not be established clearly. The extent to which high fluorides in their drinking water was related to these dental changes could not be determined. Some of the children had lived elsewhere before moving to Ft. William and could have been exposed to fluorides from some other source of drinking water of unknown fluoride content. This emphasizes the potential ambiguity of data that may depend on changes in teeth without documentation of the source and amount of fluoride responsible for the dental changes.

Additional data showing fluoride effects in man were collected in industrial work areas and in laboratory investigations where urinary fluoride levels were studied. From these investigations, guidelines for allowable levels of urinary fluorides have been determined. Levels of urinary fluoride up to about 4 ppm are acceptable regardless of the source of the exposure. So far there has been only one report relating fluorides in the ambient air in a community to indicate the occurrence of related urinary fluoride levels as high as 4 ppm.(4365)

The kind of fluoride-induced bone changes that are revealed by X-ray examinations (increased radioopacity) have been used as a guide for fluoride effects in surveying the residents of several communities. Whenever this type of fluoride-induced change was found in such surveys, the related fluoride exposures were found to have come from (a) excessive fluoride levels in drinking water, or (b) occupational fluoride exposures. Exposure to an outcropping of phosphate rock in North Africa represents an exception to the above. Dust from this natural source caused extensive contamination of drinking water and foods in the homes of nearby residents and resulted in some bone changes.(4366)

Background information on fluorides in ambient air indicates the normal level to be less than 0.24 ppb or 0.2 microgram per cubic meter ($\mu g/m^3$); the fluoride measured was probably all particulate.(4370) In some cities values of 2.3 ppb or 1.9 $\mu g/m^3$ have been observed and reported as particulate fluoride.(4371) Gaseous fluoride must have been a small fraction of the fluoride in the air since no damage to vegetation was found. In any case, the potential for these levels to cause fluoride effects in man is negligible. In a recently published, totally independent study by the National Academy of Sciences, the same conclusion was reached.*

The highest ambient fluoride concentration reported was from testing of rocket engines using fluorine as an oxidizer. In connection with one such testing program at the NASA-Lewis Research Center, a fluoride scrubber was designed to capture the reaction products, primarily HF, that result from static engine tests. From preliminary tests for the scrubber, it was predicted that "where full advantage is taken of the prevailing atmospheric conditions and stack dispersion of the gases, concentrations of hydrogen fluoride as high as 10,000 ppm may be safely tolerated."(4367) Static tests are usually very brief but, even so, 10,000 ppm is not really safe unless the dilution in the atmosphere is very rapid. No data have been found revealing the total quantity of fluorine used in this kind of testing, but it is anticipated to be relatively small.

5.4 ETCHING OF GLASS

Many publications refer to etched or frosted windows of buildings in areas adjoining processes suspected of excessive releases of fluorides. In virtually all instances, the etching was completed before it was given any attention. In these cases, etching is the result of a condition that has occurred at some previous time; and direct investigation of the cause is no longer possible. Some experiments have been performed in which levels of HF were maintained in fumigation chambers primarily to test groups of flowers and small trees. As a secondary experiment, some panes of glass were also included.(4360) The experimental results were: (a) definite etching resulted from an exposure totaling 9 hours at a level of 590 ppb, and (b) pronounced etching resulted from an exposure totaling 14.5 hours at a level of 790 ppb. These levels at which glass was etched by HF are high enough to have caused extensive damage to many species of vegetation if those levels prevailed in the fields around buildings where fluoride etching of glass has been observed.(4360)

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*"Fluorides" National Academy of Sciences, Washington, D.C. 1971, Committee on Biologic Effects of Atmospheric Pollutants. "Current Knowledge indicates that airborne fluoride presents no direct hazard to man, except in industrial exposure. However, through the commercial, esthetic and ecologic functions of plants, fluoride in the environment may indirectly influence man's health and well being."

5.5 EFFECTS OF FLUORIDES ON STRUCTURES

In the absence of water, HF forms a passive coating on steel. Highly concentrated HF solutions (above 60%) and anhydrous HF are handled in steel lines and containers. It is recommended that steel not be used when concentrations of HF are below 48% in aqueous solutions. These considerations are limited to process streams in which HF is being manufactured. Many other process streams have comparatively low concentrations of fluorides, and the materials of construction will most likely be determined by some other constituent in the process stream such as sulfuric and phosphoric acids.

At relatively low concentrations of fluorides in emissions from fluoride processes, 1000 ppm or less, the damage caused by fluorides is limited mostly to glass and brick. Etching of windows has been discussed above. Occasionally, damage to the interior brick lining of a stack has been attributed to fluorides in the emissions from an industrial process. In the furnaces used for baking carbon anodes for aluminum reduction cells, fluoride damage occurs to the high-silica brick used in the furnace walls.

6. MEASUREMENT TECHNOLOGY

An inventory and evaluation of the technology for measurement of the fluoride content of process streams has been performed. The results are discussed in the following sections under the categories of sampling, separation of fluoride from interfering ions, and analytical methods.

6.1 SAMPLING

6.1.1 Sampling Procedures

Selection of a sampling technique for measuring the fluoride content of effluents from process sources is dictated by the effluent stream composition and the pollutants to be determined. For sources that emit both particulate fluorides and gaseous silicon tetrafluoride and hydrogen fluoride, chemical reactivity presents a major sampling problem. Such sources include the industrial plants manufacturing phosphate fertilizer, producing pig iron, processing iron and steel, reducing aluminum ore, and manufacturing glass and ceramics. For accurate sampling of effluent and differentiation between particulate and gaseous pollutants from such operations, the sampling technique must prevent interaction of the gaseous and particulate fluorides.

Sampling procedures for use in the measurement of fluorides in the atmosphere have been developed to prevent, to some extent, the interaction in the collection train of gaseous and particulate fluoride. Unfortunately, except for work carried out for the Office of Air Programs (formerly the National Center for Air Pollution Control) by Dorsey and Kemnitz,(304) Elfers and Decker,(225) and the Manufacturing Chemists Association, no detailed methodology (other than APCO Procedure H-7, Reference 304) is available in the open literature covering stack sampling for fluorides. The developed techniques involve the sampling of stack effluents with a hot glass probe followed by a heated train consisting of a cyclone, filter and a Greenburg-Smith impinger containing distilled water. Particulate fluorides are collected using a high-efficiency cyclone followed by a Whatman No. 41 filter. Active gaseous fluorides, such as HF and F_2, react with the heated glass probe to form gaseous silicon tetrafluoride which, after passing through the heated cyclone and filter, hydrolyzes in the water of the

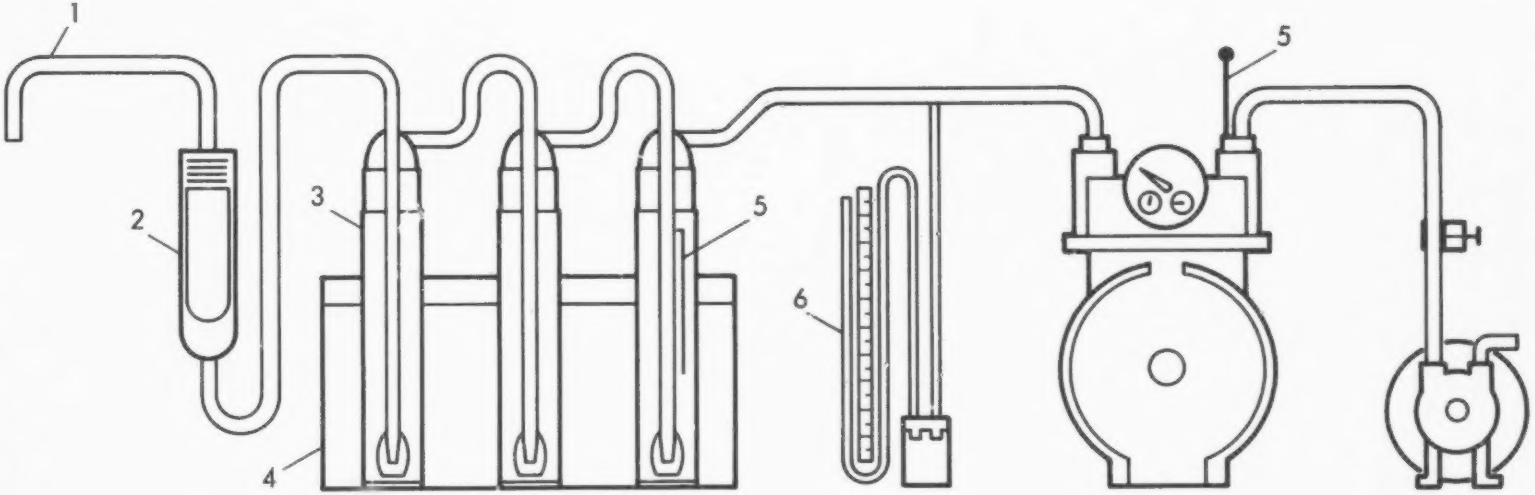
Greenburg-Smith impinger to form fluosilicic acid and insoluble orthosilicic acid. The water-soluble particulate fluorides, total particulate fluorides, and soluble gaseous fluorides can thus be determined separately.

Some of the procedures used for sampling fluorides in ambient air may be adaptable for sampling fluoride emissions from cyclones, baghouses, electrostatic precipitators, or other so-called dry collection equipment. At least the gaseous portion of the fluoride emissions from these collectors might be adequately measured. The procedure using sampling tubes with alkaline coatings could be used if a suitable dilution technique were employed. However, the emissions from scrubbers using aqueous scrubbing liquids require other measurement methods. Water vapor, droplets of entrained scrubber liquid, and uncaptured fluoride particulates could all be present at the scrubber exit. Considering these problems, even the sampling of particulate was viewed with concern by Lunde(870) who stated, "Adequate data are not available to evaluate the performance of the equipment installed for the collection of particulate fluorides." His comment refers to scrubbing devices using liquids to capture fluorides.

The most important constituent, the gaseous fluoride emission from the scrubber, is the constituent most difficult to separate from such a mixture. Total fluorides could be analyzed very efficiently, but the ambiguity concerning the proportion of gaseous and particulate fluoride in the emission would remain.

6.1.2 Performance of Sampling Trains

Mixtures of fluorides are usually evolved by industrial processes. If there is a need to separate the particulate and gaseous fluoride components, the sample train shown in Figure 6-1 has frequently been used for this purpose. The particulate filter shown is a porous thimble. A variety of filters and filter holders have been used. Some portion of the sample may deposit on the inner surfaces beginning at the probe; therefore, to minimize the reaction of HF with the sample train, stainless steel parts have been used. As particulates collect on the filter surface, the dust layer tends to become a collector for gaseous fluorides. Many dusts will absorb or adsorb HF to some degree, and two patents extol the effectiveness



The components are: (1) sampling probe; (2) dry filter; (3) impinger (dust concentration sampler); (4) ice bath container; (5) thermometers; (6) mercury manometer; (7) Sprague dry gas meter; (8) vacuum pump; and (9) hose clamp to control gas flow rate.

Figure 6-1. Schematic Diagram of Sampling Train for Dry Particulate Matter

of aluminum oxide for retaining HF.(4309, 4168) Limestone dust is well known for its ability to remove HF from air; however, little has been published on the reactivity of HF with dusts such as fly ash from coal burning, borates in glass making, and clays or other mineral dusts present in industrial processes. It seems clear that in a sample train such as that shown in Figure 6-1, the filtering section would collect a particulate sample with an indeterminate portion of the gaseous fluorides either reacted or adsorbed. The aqueous collectors would retain the remaining gaseous fluoride.

Citric acid-treated filter paper allows gaseous fluoride to pass through to be collected in a following section of the fluoride sampler. The effectiveness of this arrangement for stack sampling would be completely dependent on very small dust loading of the filter; therefore, it is not a promising method for sampling most industrial effluent gas streams which contain appreciable amounts of dust.

Other sampling trains have included insertion of a small cyclone collector ahead of the filter to trap dust larger than 25 microns, reducing the amount of dust deposited on the surface of the filter. The filter has, in some cases, been placed in the train following the aqueous collectors.

Where the quantity of particulate matter in an effluent stream is large, the separation of gaseous and particulate fluorides is difficult. However, control techniques are frequently concerned only with the determination of total fluoride content. The Greenburg-Smith impinger can be considered as the standard for collecting total fluoride though other collectors are sometimes used. As reported in a review by Farrah,(2015) the Greenburg-Smith impinger is fairly rugged and has collection efficiencies ranging from 90 to 98% when operated properly, at flow rates of 1.5 to 2.0 cfm.* Pack, et al,(906) and Farrah(2015) report that pure water is as good a collector as caustic solution for fluoride contaminants. The impinger collection solution is usually diluted to a constant volume and an aliquot taken from this solution for determination of the fluoride content by the separation and analytical method selected.

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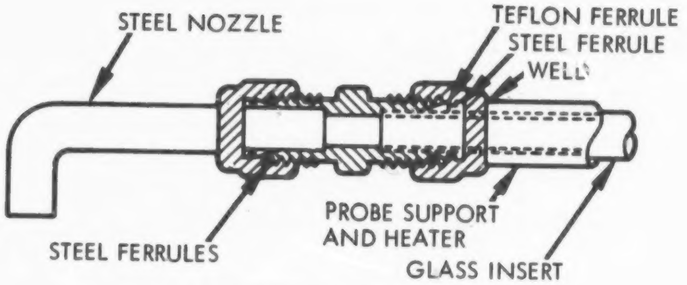
*Keenan and Fairhall(4308) found that lead fume particulate collection efficiencies improved when a flow rate of 1.6 cfm was used with a standard impinger designed for use at a flow of 1 cfm.

Using the hot glass probe sampling technique, the particulate contaminant (free of gaseous fluorides) is transferred quantitatively from the cyclone and probe by washing with acetone after which the particulate material is dried and weighed. The particulate contaminant collected on the filter paper is combined with the cyclone-collected particulate material; the filter paper is shredded; and the contents are diluted to a constant volume. If, upon acidifying, the particulate material is not dissolved, caustic fusion as described by Pack, et al(906) is required for complete recovery of fluoride. Aliquots are taken to yield the desired quantity of fluoride for the analytical method selected.

If the reactivity of gaseous fluorides could be diminished by some mechanism, difficulties in separating them from dusts could be reduced and fluoride sample collection simplified. Since SiF_4 is less reactive than HF and since HF can be converted to SiF_4 through contact with heated glass, this principle was employed in designing the sample train shown in Figure 6-2. This sampling train, developed by Dorsey and Kemnitz,(304) modified by Elfers and Decker(225) and described in APCO Procedure H-7, provides, with some limitations, detailed methodology for handling the total range of fluoride contaminants in most process effluent streams and for differentiation between particulate and gaseous fluorides in stack gases. Potential problems with this sampling train still await solution. Gelatinous silica hydrate is formed by the SiF_4 hydrolyzed in the impinger(340) solution. A similar problem with gelatinous silica was solved by using ammonium compounds.(4157) Whether SiF_4 would react with iron oxide dust on the surface of the filter may need to be tested; iron oxide is reported to react readily with SiF_4.(4310) In some process gas streams, the heated probe could become coated with dust, carbon, or tarry materials to such an extent that the desired reaction of HF with glass could not occur.

The technique developed by Pack, et al(906) involving use of a glass fiber filter for collection of suspensoid particulate contaminants can be used instead of the cyclone and heated glass probe. The glass fiber or paper filter (which separates and collects 98% of the suspensoid particulate material) can be washed to remove soluble particulate fluorides. Filter discs treated with alkaline reagents, used instead of a complex sampling


STEEL NOZZLE
TEFLON FERRULE
STEEL FERRULE
WELD
STEEL FERRULES
PROBE SUPPORT AND HEATER
GLASS INSERT

COMPRESSION FITTING

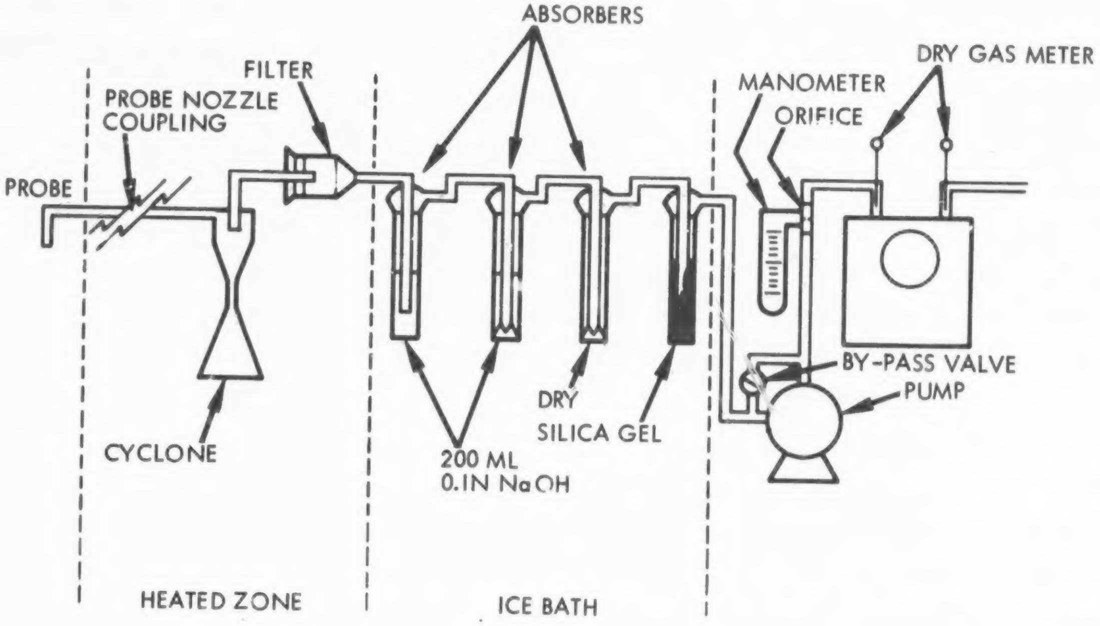

ABSORBERS
DRY GAS METER
FILTER
MANOMETER
PROBE NOZZLE COUPLING
ORIFICE
PROBE
BY-PASS VALVE
PUMP
DRY SILICA GEL
CYCLONE
200 ML 0.1N NaOH
HEATED ZONE
ICE BATH

Figure 6-2. EPA Sampling Train

train, will also collect total fluorides very satisfactorily. However, some limits on the size of the fluoride sample collected may have to be observed to avoid exceeding the capacity for absorption of the filter while collecting a relatively large sample compared to the intrinsic fluoride content of the glass fiber. Micropore-type filters may be used to collect most, if not all, submicron-size particulate fluorides.

6.1.3 Process Factors Affecting Sampling

Some factors contribute to the sampling problems and are described on an industry-by-industry basis.

The phosphate industry uses phosphate rock as raw material which can cause problems because the rock does not have a fixed composition but varies from mine to mine and even from area to area within the same mine. Some phosphate rock behaves as though much of the fluoride was present as fluosilicate and some as fluorspar. Since the raw materials are treated differently in different processes, the form of the fluoride may be very important.(4265) Heat may be added as in nodulation, with SiF_4 released from the fluosilicate present; or acidulation may be used as in fertilizer manufacturing with the SiF_4 escaping but the HF derived from CaF_2 staying in the slurry to react with some of the calcium carbonate; or heat, acid, and silica may be added to the raw material as in the manufacture of defluorinated rock with nearly all of the fluoride volatilized, probably as a mixture of SiF_4 and HF. In each instance, some pulverized phosphate rock may be entrained in the effluent gas stream along with the volatilized fluoride and water vapor released by the process reactions. Each of these mixtures of fluorides may react differently as it is drawn into and through the sampling train.

Little has been published describing fluoride effluent gas streams related to iron and steel manufacturing. However, it is reasonable to assume that: (a) fluorides added to the slag in steel furnaces may react with moisture to release HF, (b) fluorides may be converted to fluosilicates in the slag and then thermally decomposed to release SiF_4, and (c) fluorides may sublime as iron fluorides since the sublimation temperature (1800° to 2110°F) is well below the pouring temperature of steel.(4310) The complexity of these reactions in the presence of dusts and moisture in the effluent gases could make sample collection very complicated and the analytical results difficult to interpret. As little as half of the fluoride added in steel furnaces is recovered in the slag from the steel processing.(4276)

The nature of fluoride evolution in aluminum reduction is complex with HF, cryolite, alumina, aluminum fluoride, chiolite, and possibly heavy hydrocarbons in the effluent gas from the aluminum reduction processes. The evolution mechanisms for these materials have not been completely described but fragments of the chemistry have been reported.(4310, 889, 4163) Aluminum fluoride dispersed as a fume in air reacts with moisture to form HF and aluminum oxide, but the rates of reaction are dependent upon vapor pressure(4163) and temperature.(889) Hence, as aluminum fluoride leaves an aluminum reduction cell, hydrolysis starts as soon as it encounters atmospheric moisture but diminishes rapidly as the fume cools. Cooling may occur rapidly enough from some or much of the aluminum fluoride to remain dispersed in the effluent gas stream as an unhydrolyzed fume. Sublimed chiolite may rearrange into other solids as it condenses but in cooling probably gives rise to a fine fume that reacts slowly or not at all with moist air at ambient temperatures. Over the range of water vapor pressure and temperatures that prevail in the fluoride collection systems used in aluminum plants, there has been no really complete description of the chemical and physical states of the fluoride to be sampled at various points in emissions control systems.

6.1.4 Sampling Summary

Several of the devices for collecting fluorides from effluent streams have been discussed. Some of them performed very well in sampling fluorides dispersed in ambient air and separate gaseous and particulate fluorides. For sampling industrial gas streams, too little testing has been done to demonstrate the usefulness of these devices for fluoride levels that may be far higher than those found in ambient air.

The types of sampling trains frequently used for stack sampling have been discussed in relation to industrial fluoride effluent gas streams. Since these effluent streams are usually mixtures of gaseous and solid fluorides, separation of the two phases causes problems in sample collection. Particulates deposit on the interior surfaces of probes and sampling tubes. This dust and that collected on the surface of the filter in the sampling train may absorb or adsorb significant amounts of gaseous fluorides. Reactivity of gaseous fluorides with the sampling train components may further interfere with the separation of the fluorides into gaseous and particulate samples.

Inaccuracies related to fluoride sampling and analysis of process streams are primarily caused by procedures used for collecting samples. The materials that are collected can be analyzed relatively accurately for fluoride content.

6.2 FLUORIDE SEPARATION

Before determining fluoride in particulate and gas fractions collected from effluents, interfering ions must be removed if any of the well-established analytical methods are to be used. Only aliquots providing the quantity of fluoride for the analytical method selected should be used in order that fluoride isolation can be performed with a minimum of work.

The separation of the fluoride ions from ions interfering in fluoride analyses such as Al^{+3}, PO_4^{-3}, Cl^-, SO_4^{-2} is accomplished by (a) distillation, (b) ion exchange, or (c) diffusion. The most widely used of the separation methods is the Willard-Winter(4311) distillation. This method on the macro-scale is considered the standard by which newer methods are evaluated. Fluorine is separated as fluosilicic acid from interfering ions by steam distillation from solutions containing perchloric,(4312) sulfuric,(4312,4313) or phosphoric acids.(4314) The fluosilicic acid is swept out of the distillation flask with water vapor, the boiling point of the solution being held at a constant temperature by addition of steam or water and by regulating the heat applied to the solution. The addition of steam rather than water reduces the time required for the distillation and eliminates bumping of solution.(4315) When the original sample is relatively free of interfering materials and the fluoride is in a form easily liberated, a single distillation from perchloric acid is carried out at 135°C. Samples containing appreciable amounts of aluminum, boron, or silica require a higher temperature and larger volume of distillate for separation. In this case a preliminary distillation from sulfuric acid at 165°C is commonly used. Large amounts of chloride are separated by precipitation with silver as an intermediate step. Small amounts of chloride are held back in the second distillation from perchloric acid by addition of silver perchlorate to the distilling flask.(2015) The distillation method requires considerable operator time and results in a large volume of distillate for quantitative recovery (250-375 ml for samples containing up to 100 mg of fluoride).

Isolation by an ion exchange resin allows recovery of fluoride in a more concentrated form free of interfering ions. Nielsen and Dangerfield(4316) separated microgram quantities of fluoride on a quaternary ammonium styrene resin with recoveries approaching 95% for amounts of 20μg or less from mixtures including hydrofluoric acid, sodium fluoride, fluosilicic acid and calcium fluoride. The technique was used to concentrate Willard and Winter distillate, and was also used directly on impinger-captured atmospheric fluorides. Newman(4317) removed interfering anions as well as cations on a single exchange resin (Di-Acidite FF). Funasaki, et al, (164) removed interfering ions PO_4^{-3}, AsO_4^{-3}, SO_4^{-2}, and CO_3^{-2} by means of Amberlite IRA-400. Elution was affected with 10% NaCl. Dowex anion exchange resin was used by Ziphin, et al,(4318) to separate fluorides from PO_4^{-3} with gradient elution of the fluoride from the resin by sodium hydroxide. Nielsen(4319) separated fluoride from Fe^{+3}, Al^{+3}, PO_4^{-3}, and SO_4^{-2} on the resin and removed the ions by stepwise elution with sodium acetate.

The ion exchange columns permit separations of 1 μg to 0.1 g of fluoride from interferences when the sample is in a few milliliters up to a liter of solution. The elution volumes usually are about 50 ml.

Diffusion methods for separating fluoride from interferences before determinations are simple and show great promise. They involve collection of fluoride in volumes ranging from a few milliliters to a liter of alkaline solution, the liberation of fluoride by treating with mineral acids, diffusion through a short distance and absorption of the fluorides in approximately 5 milliliters of alkaline solutions. These methods are generally applicable to quantities of fluorides in the 0.05 μg to 1 mg range. Singer and Armstrong(4320) and Hall(4321) suggested the use of polyethylene bottles for diffusion vessels which were sealed with stoppers. Alcock(4322) prepared a satisfactory diffusion cell of Teflon that was used at 55°C;

higher temperatures released fluoride from Teflon. Taves(4323) found that fluoride passes into trapping solutions in the form of methylfluorosilane if silicone grease is used for sealing the diffusion cell. In the presence of the simplest silicone, hexamethyldisiloxane, the separation of fluoride is much more rapid. A faster diffusion method for the separation of fluoride was proposed;(4324) fluoride was liberated in the presence of hexamethyldisiloxane in 6N hydrochloric acid. The separation was carried out at 25°C for 2 to 6 hours, depending on the volume of sample analyzed. Otherwise, the separation by diffusion takes place for at least 24 hours at much higher temperatures (usually 60°C). Tusl(4325) established a rapid diffusion technique using polyethylene diffusion cells to which were added a purified high vacuum silicone grease that was a homogeneous mixture of methylsilicone fluid and aerogel of silica. Following the diffusion separation, fluoride was determined by the zirconium - SPADNS colorimetric method. Stuart(4326) followed the diffusion separation with fluoride determination with the fluoride specific ion electrode. He isolated 0.05 μg - 200 μg from a large volume of solution to a 5-milliliter solution.

Because of its wide acceptance and ability to effect satisfactory separations of fluoride with a minimum of equipment, the Willard-Winter distillation technique is recommended for separating interfering ions in the wide weight range from 0.1 μg - 1 g of fluoride collected from plant gaseous effluents. The distillation procedure described in Procedure H-7 appears satisfactory for most applications. Though the ion exchange isolation of 0.1 μg - 1 mg fluoride from samples collected from the atmosphere is useful, there appears little need for this technique for use with samples from plant effluents because of the larger quantities of fluoride in the samples. For handling a large number of samples, the diffusion separation techniques are capable of isolating fluoride from interferences and concentrating it into 5 milliliters with the possibility of labor savings.

6.3 ANALYTICAL METHODS

Analytical methods are discussed in several sections as indicated below:

- Spectrophotometric
- Titrimetric

- Instrumental
- Continuous and semicontinuous

As previously noted, aliquots from the samples collected should be subjected to some process for separation of fluoride from interfering ions. The aliquots to be taken for most efficient separations should be only as large as those required by the selected analytical method. For the most accurate analyses, the aliquot should provide a mid-range fluoride concentration for that method. Examples of the fluoride concentrations found in various stack effluents are listed in Table 6-1. Table 6-2 gives the applicable concentration ranges for the various analytical techniques described. The concentration ranges in the table and the following discussions are for solutions containing fluoride ions after separation from interfering ions.

6.3.1 Summary of Analytical Methods and Recommendations

The spectrophotometric methods have been developed to the point where several are accepted as standards. After the separation of soluble fluorides from interfering ions, spectrophotometric methods can generally be used to determine fluoride with a relative precision of 5 to 10% for solutions containing 0.01 μg to 0.2 mg of fluoride per milliliter. The claim in some publications of better precision is largely unsubstantiated. The accuracy, except on standard solutions containing NaF, has not been established but should be about the same as the relative precision for solutions that do not contain any interfering ions. Little or no data exist concerning total system accuracy, i.e., sampling, collection, removal of interfering ions and spectrophotometric analysis.

Titration methods using indicators to detect the end-point are all difficult to perform with a high degree of precision and have been superceded, to a major extent, by the use of the specific ion electrode to determine fluoride ion content either directly for relatively dilute solutions, or by the use of titrimetric methods employing a specific ion electrode for end-point determination.

Table 6-1. Concentration of Fluoride Found in Various Effluents (At standard temperature and pressure)

	Grains/ft^3	w/v mg/M^3	v/v ppm
NORMAL SUPERPHOSPHATE			
Den Scrubber Emissions	0.08-0.30	183-686	220-824
nominal	~0.15	343	412
Building Scrubber Emissions	~0.00035	0.80	0.96
DI-AMMONIUM PHOSPHATE			
Granulator Exhaust	0.0093	21.3	25
Dryer Duct	0.1100	250	300
Dry Screens Exhaust	0.0025	5.7	6.8
WET PROCESS PHOSPHORIC ACID			
AP-57			
Digester-Filters-Tanks	0.0011-0.0147	2.5-33.6	3-40
Scrubber Exhaust "Big Plant"	0.001-0.03	2.5-68.6	3-82.3
Scrubber Exhaust "Medium Plant"	0.0048	10	12
TRIPLE SUPERPHOSPHATE			
Scrubber Inlet	0.55	1258	1500
Scrubber Outlet	0.016	36.6	43.9
Den Scrubber Inlet	0.10	229	275
Den Scrubber Outlet	0.008	18.3	22.0
Reactor and Granulator Scrubber Exhaust	0.0021	4.8	5.8
Dryer	1.3	2970	3560
Dryer Exhaust	0.0025	5.7	6.8
Granulator Scrubber Inlet	0.48	1098	1320
Granulator Scrubber Outlet	0.030	68.6	82.3
DEFLUORINATED PHOSPHATE ROCK			
Kiln Scrubber Exhaust	0.00056	1.3	1.6
Fluosolids Scrubber Exhaust	0.0048	11.0	13.2
Prep. Feed to Kiln	0.00095	2.2	2.6
Di-Cal (from acid and limestone)	0.00020	0.5	0.6
ELEMENTAL PHOSPHOROUS			
Water Sol. F(updraft dryer)	0.0313	71.6	85.9
Emissions Particulate (updraft dryer)	0.0099	22.9	27.5
Furnace Exhaust Gas	0.0031	7.1	8.5
ALUMINUM PREBAKE ANODE			
Primary Control Process (average)	0.033	75.5	90.6
Secondary Control Process	0.00006-0.00042	0.13-0.96	0.16-1.16
ALUMINUM VERTICAL STUD SODERBERG			
Primary (average)	0.43	982	1180
Secondary Loading	0.00049	1.12	1.34
ALUMINUM HORIZONTAL STUD SODERBERG			
Primary (average)	0.01	22.9	27.5
Secondary Loading	0.00026-0.00042	0.59-0.96	0.71-1.15
IRON AND STEEL			
SINTER PLANT			
Normal Conditions, water sol. F	0.0023	5.3	6.4
Normal Conditions, particulate F	0.0011	2.5	3.0
Special Conditions, water sol. F	0.0042	9.6	11.5
Special Conditions, particulate F	0.00075	1.7	2.0
Blast Furnace Stoves	0.0027	6.1	7.3
Boiler House	0.00014	0.32	0.38
Coke Ovens	0.00068	1.6	1.9
Open Hearth, water sol. F	0.0157	35.9	43.1
Open Hearth, particulate F	0.00004	0.09	0.11

Table 6-2. Applicable Concentration Range of Analytical Methods

Technique	Applied to Aliquots of Fluoride Concentration Range	Precision	Interferences**	Comments
FLUOROMETRIC				
Morin or quercetin	0.5-20μg	±5%	Fe^{+3},$C_2O_4^{-2}$,Cl^-,Mn,NO_3	Better accuracy is claimed for these methods than for visual end-point techniques for concentration above 2mg.
Specific ion electrode	0.02μg/ml-20 mg/ml (5 ml minimum sample)	±1%	OH^- total ionic strength	Preferred method of end-point detection in most cases. Precision is better than other titrimetric procedures.
INSTRUMENTAL				
Specific ion electrode	0.03μg/ml to 30 mg/ml	5% standard deviation at low range, 2% at high range	OH^-,Al^{+3},Fe^{+3},pH adjusted	Ease of use and equal precision justifies use in most cases in place of spectrophotometric methods.
Kinetic method	0.0004 μg-0.4 mg/ml	Not established research method	SO_4^{-2},Cl^-,Al^{+3},PO_4^{-3}	Research method.
Atomic Absorption	0.005 μg/ml-4 mg/ml	~5% standard deviation	SO_4^{-2}, PO_4^{-3}	Can be used over a wide concentration range. Useful when a large number of samples are to be analyzed.
X-Ray of LaF_3	1μg-apx 10mg	~5% standard deviation	None	Research method that can be developed into a rapid method.
Radio-release of zirconium salt	10μg-100 g	~5% relative precision	PO_4^{-3},Fe^{+3},Al^{+3}	Research method.
Amperometric	0.5μg/ml-10 μg/ml	Not established	None	Research method; could be used to detect titration end-points.
Photo-activation	0.01%-5% in mg size samples (dried)	~5% relative precision	Cl,Br,S	Useful for small samples.
Mass spectrometric	0.1 mol%-100 mol% for Hf,SiF_4,CF_4,C_2F_6	~5% relative precision	None	Determination of HF difficult, useful for determining organic bound flourine.
Electrochemical				
Null point measurement of cerium (IV) to (III)	10μg/ml-1 mg/ml	None given	Al^{+3},Fe^{+3},PO_4^{-3}	Research method.
Coulometric	0.001μg/ml-100 μg/ml of F_2	None given	None	Specific method for F_2.
Gas Chromatography	1mg/cc-100% as HF or SiF_4 in gas sample	~5% relative precision	None	Could be developed into an automatic method.
SPECTROPHOTOMETRIC*				All the spectrophotometric methods suffer from interferences from ions that form more insoluble compounds with the metal of the complex than the fluoride itself. pH changes also effect most of these methods.
Lanthanum-Alizarin Complexone	0.01-0.4μg/ml	±5%	$PO4^{-3}$,Al,Cl^-,Fe,NO_3^-, $C_2O_4^{-2}$	Nitrate and phosphate interfere only when in excess.
Titanium-Chromatropic Acid	2μg-0.2mg/ml	±5%	PO_4^{-3},Al,Fe,$C_2O_4^{-2}$ (SO_4^{-2} in excess)	Sulfate does not interfere. K^+,Na^+,NH_4^+,Cl^- and NO_3^- do not interfere in small amounts.
Iron-Ferron	0.01-0.2 mg/ml	±5%	PO_4^{-3},Al,Fe,oxalate, SO_4^{-2}	Useful at higher fluoride concentration levels.
Thorium-Alizarin	0.01μg-0.2 mg/ml	±5%	PO_4^{-3},SO_4^{-2},Al,Fe, oxalate	Calibration not linear at higher fluoride concentrations.
Zirconium-SPADNS	0.01μg-0.2 mg/ml	±5%	PO_4^{-3},Cl^-,Al,Fe,oxalate	Calibration not linear at higher fluoride concentrations.
Amadac-F	0.5-4μg/ml	±5%	PO_4^{-3},Cl^-,Al,Fe,oxalate	Affected by high acid or alkali content, pH change, and total ionic strength.
Zirconium-Eriochromcyanin R	0.01μg-0.2 mg/ml	±5%	PO_4^{-3},Cl^-,Al,Fe,oxalate (SO_4^{-2} in excess)	Calibration is linear from 0.01-2μg/ml.
TITRIMETRIC				Thorium nitrate is usually preferred as titrant. Lanthanum is also used in some cases.
Visual				
Purpurin sulfonate	1μg-10 mg	>±5%	PO_4^{-3},SO_4^{-2},Al,Fe,$C_2O_4^{-2}$	
Alizarin Red S	1μg-10 mg	>±5%	PO_4^{-3},SO_4^{-2},Al,Fe,$C_2O_4^{-2}$	Listed in order of preference as indicators.
Eriochromcyanin R	1μg-10 mg	>±5%	Fe,oxalate,Cl^-,Mn,NO_3, etc.	
Photometric				
(Same metal-dye complexes can be used)	1μg-100 g	±5%	Same	Technique requires a colorimeter and is slower than visual end-point; however, operator error is reduced.

*Accuracy is not known for most methods except for standard solutions where the accuracy is the same as the precision.

**Interferences usually removed by distillation, ion exchange or diffusion.

6.3.2 Spectrophotometric Analysis

Interaction of fluoride ion with a metal dye complex generally forms the basis for the colorimetric-type methods. The metals of the complex are from the group Th, Zr, La, Ce, Y, Bi, Fe, and Al. This group is capable of forming insoluble or slightly ionized fluorides and also insoluble phosphates which is a well-known interferent. Some of the more common dyes used for this purpose are Alizarin Red S, Eriochrome cyanine R, arsenazo, Ferron, and SPADNS. Many of these dyes function as acid base indicators and, therefore, require close control of pH in fluoride determination.(2015)

Many semi-quantitative and qualitative techniques have been used for estimation of fluoride; while these are not spectrophotometric, they are colorimetric and a typical example is discussed here. Mavrodineauu(879) describes a color complex for fluoride ion sample on dry zirconium or thorium nitrate and a lake-forming dye (sodium alizarin) absorbed on filter paper. No interference was noted for other halogens, but sulfate and phosphate interfered. Semi-quantitative results could be achieved by acid treatment and color intensity comparison.

Many color complex systems for the determination of fluoride spectrophotometrically have been described in the literature. Generally, spectrophotometric methods provide a means for measuring a 20,000 fold range of fluoride concentration directly with very good sensitivity. Ranges for two common systems are reported as follows: Iron-Ferron, 0.01 - 0.2 mg/ml (1 cm cell) and 0.01 - 0.4 μg/ml for Lanthanum-Alizarin "Complexone" reagents. Both these systems have visible spectrum absorptions. Belcher and West(4327) report 200% increases in sensitivity by working in the ultraviolet region of the electromagnetic spectrum.

Decolorization of Titanium-Chromotropic acid by fluoride ion with a detection level of 2 μg/ml (total range 2 μg to 0.2 mg per ml) was proposed by Babko and Khodulina.(4328) No interference was observed from sulfate, but phosphate must be removed. Sensitivity to pH is a problem common to this technique. If a dye is added to the system, the resultant color change can increase sensitivity to <0.5 μg/ml. Skanavi(648) applied this method to micro quantities of fluoride with a sensitivity in the range 0.3 to 17 μg per ml; however, accuracy was not too good in this range. Phosphate interferes, but K^+, Na^+, NH_4^+, $SO_4^=$, Cl^-, and NO_3^- in small amounts do not cause problems.

Mal'kov and Kosareva(4329) outlined a method using thorium-alizarin to form a colored complex with fluoride. Range of the method is 0.01 μg to 0.2 mg fluoride per milliliter.

Amadac-F sold by Budick and Jackson Laboratories(4330) is a mixture of alizarin complexan, lanthanum nitrate, acetic acid, partially hydrated sodium acetate and stabilizers useful for quantitative determination of fluoride in the range 15 - 50 μg per milliliter. A color change is observed in this reaction complex which is affected by high acid or alkali content, pH change, and total ionic strength.

Green iron-Ferron complexes with fluoride to produce a color change useful for fluoride measurement in the range 0.01 - 0.2 mg/ml. Adams(4331) in discussing this work proposed the use of this method for stack monitoring with removal of sulfur dioxide, an interferent, by sodium tetrachloromercurate absorber solution. A prior reference(694) utilized airconium-Eriochrome cyanine R for the determination.

A recent spectrophotometric technique described by West, Lyles, and Miller(4332) analyzes fluoride by complexing with alizarin complexan and lathanum buffer. Determinations in the range 0.01 - 0.4 μg/ml can be done if metals, nitrates, and phosphates are removed. That is, concentrations of <4 μg/ml nitrate and <3 μg/ml phosphate in 0.4 μg/ml of fluoride are tolerable.

Because of the large volume of literature and numerous possible combinations of metal-dye-fluoride complexes, the above summary must be considered only as a few typical recognized procedures which reflect the possibilities of the spectrophotometric technique. The methods described here generally can be considered as new techniques or the latest modification of older techniques. It is very difficult to make a statement of preference for any of these methods unless dynamic range of applicability of specific interference are the judgment criteria. Sensitivity and precision are nearly the same for each method.

6.3.3 Titrimetric Analyis

The most commonly used titrants for the volumetric or titrimetric determination of fluoride in aqueous systems are thorium and lanthanum nitrate. However, because of the large variety of end-point detection procedures the classification of the titrimetric methods will be based on the detection technique utilized. End-point detection can be generally broken down into the following types: visual, photometric, fluorometric, specific ion electrode, and electrometric. While specific ion electrodes may be classed under electrometric, their relative importance dictates a separate class for this discussion. The first four types will be evaluated in this section, where titration of the total sample distillate, thus preventing dilution error, is possible.

The visual end-point detection procedures have generally been supplanted by other means for end-point detection and by spectrophotometric methods. Photometric, fluorometric, electrometric and specific ion electrode end-point detection have largely eliminated the operator perception and dilution errors present in the visual methods.

6.3.3.1 Visual

The greatest difficulty in the quantitative utilization of the color indicator end-point techniques for fluoride is that it depends on the color perception and experience of the operator. Many indicators have been suggested for improving the subtle color change; however, there still remains much to be done. Much work has been done by Willard and Horton(4312) on these as well as other systems with the following colorimetric indicators being recommended: Purpurin sulfonate, Alizarin Red S Eriochrome cyanin R, dicyano-quinizarin, and Chrome Azurol S.

In visual procedures the sample of fluoride is titrated with thorium or lanthanum nitrate to the end-point as indicated by one of the suggested complex colorimetric (visual) dyes. Generally the methods using visual indicators to detect the end-point are used in the fluoride concentration range of 1 μg to 10 mg in an aliquot from 10 to 200 ml. Analysis in this range is described in ASTM Method D1606-60.

Not only do these titrations suffer from the above mentioned operator error, but other problems exist depending on the composition of the sample to be analyzed. When large amounts (above 1 mg) of fluoride are titrated, interference may result from semi-colloidal thorium nitrate, and medium-to-high concentrations of metals, nitrates, and phosphates interfere in most cases.

Allison(525) in his work, compared the determination of fluoride by both volumetric visual end-point detection and a colorimetric (spectrophotometric) method with the conclusion that the latter technique was more sensitive and should be used in the 0.5 to 50 μg/ml range, while the volumetric was faster and more useful for concentrations above 50 μg/ml.

6.3.3.2 Photometric

The real advantage in using a photometer to determine the end-point in a fluoride determination lies in the elimination of the variable of operator perception differences. All the other parameters remain essentially the same as for the visual indicator method above.

6.3.3.3 Fluorometric

Here the dyes recommended for use are different from the visual indicator dyes because of the requirement for measuring fluorescence changes to detect the end-point. Willard and Horton(4333) recommend two; pure sublimed morin and quercetin. The titration is again carried out using thorium nitrate, while the end-point is observed by the fluorescence change. Better accuracy is claimed for this method than for the color end-point method for fluoride concentrations greater than 2 mg. Many variables again need to be controlled, such as pH and interfering ions.

Willard and Horton(4333) also describe a fluorometric technique for the determination of trace amounts of fluoride using aluminum-oxine or aluminum-morin systems. In these systems the fluoride complex with aluminum decreases the aluminum-oxine or morin complex. The resultant change in fluorescence of the system is measured. The range of sensitivity to fluoride is around 0.5 to 20 μg total sample. Many variables must be controlled and standards should be run with each set of unknowns. Ions that react with aluminum or oxine or which precipitate with fluoride at pH 4.7 must be removed.

6.3.3.4 Specific Ion Electrode

The use of the fluoride specific ion electrode (lanthanum fluoride membrane electrode) for end-point detection is a recent innovation and is discussed by Lingane(4334) and Frant and Ross Jr.(4335) The conclusions reached by these and other investigators point out the usefulness of this technique. Sensitivity to fluoride over a concentration range of five orders of magnitude is easily achieved while ultimate sensitivity is down to 10^{-7} M fluoride. The electrode is very selective to fluoride, but pH and total ionic strength are very important considerations in the analysis. In typical titrations of fluoride with thorium and lanthanum nitrate, the latter yielded the best potential break with precision to ±1 mv. Far better end-point accuracy and precision were achieved using the electrode than could be achieved using color indicators for detection. The useful range of this end-point detection method is for solutions in the concentration range of 0.1 μg to 20 mg/ml.

Schultz(4336) points out that large errors can result from potentiometric titrations employing ion-selective electrodes. The error increases as the sample ion concentration decreases and as the interfering ion concentration, solubility product constant, and dilution factor increase.

Of the above mentioned end-point detection methods the fluoride electrode technique is the most precise (interference removed) and generally the easiest to apply.

6.3.4 Instrumental Methods

Nearly every analytical instrument has been investigated for direct determination of fluoride. Many of these instruments have been previously discussed as detectors for titrimetric end-points, but in this section instrumental methods are discussed as they apply to direct determination of fluoride either as collected or after separation from interferences common to most analytical methods. The various instrumental techniques are discussed below.

6.3.4.1 Specific Ion Electrode

The accepted dynamic range for the new fluoride specific electrodes is from 50 mg/ml down to 0.10 μg in the minimum usable volume of 5 ml. Preliminary work with this electrode has shown promise of making fluoride ion determinations virtually as simple, rapid, and precise as hydrogen ion activity measurements with the glass pH electrode. It must be remembered that fluoride activity is measured and concentration is dependent on total ionic strength as well as other factors.

Harriss and Williams(327) discuss the direct measurement of fluoride with the specific ion electrode and noted the speed and low cost of this analysis. Baumann(4337) describes the interference from hydroxyl ion and its elimination for accurate fluoride analysis. As little as 10^{-5} M fluoride (1 μg in 5 ml) could be analyzed with a relative error of ≃10% and standard deviation of <5%. He suggested that interfering ions be complexed before fluoride analysis. Electrode response time was less than one minute in these experiments. Durst and Taylor(4338) describe microchemical analysis techniques for fluoride using the electrode.

A comparison of the specific ion electrode to the Spadus-Zirconium method by Elfers and Decker(4265) showed good agreement between the two, but the electrode technique was much faster. Their reported detection limit was 0.2 μg fluoride in a 5 ml aliquot.

Because of the importance of the total ionic strength on the fluoride concentration measurement with the electrode and the effect of acidic or basic media on the values of fluoride, it is necessary to control or evaluate these parameters. Vanderborgh(4339) used a lanthanum fluoride membrane electrode in his study of response in an acidic solution with varying ionic strength. A recent article by Bruton(4340) for the useful range of the electrode points out that the known addition technique can be used for the simple and accurate analysis of fluoride. The millivolt readout for the electrode is adjusted to zero in the sample, an addition of standard fluoride is made, and the change in potential is related to fluoride concentration. The activity coefficient must remain constant for accurate measurement; where necessary this can be accomplished by the addition of a noninterfering salt.

Frant and Ross(4335) adjusted the total ionic strength, the pH, and complexed ferric iron or aluminum (citrate used) by using a buffer in a 1/1 ratio with the samples and standards. Fluoride could be determined accurately over the entire useful electrode concentration range using a single calibration curve for a wide range of samples.

6.3.4.2 Kinetic Method

Because a kinetic method employs unusual instrumentation, the kinetic method is included under the instrumental section. Klorkow, et al(4341) developed a kinetic method for the determination of traces of fluoride (3.8×10^{-2} - 3.8 μg/ml) based on strong inhibiting action. Fluorides act as a negative catalyst in the zirconium-catalyzed reaction between perborate and iodine. Kinetic measurements are accomplished by an automatic potentiostatic technique. Only small quantities of extraneous ions can be present.

6.3.4.3 Atomic Absorption

Bond and O'Donnell(5020) applied the depression of absorption of the magnesium line at 285.2 mμ into an atomic absorption method for fluoride in the range of 0.005 μg/ml - 2000 mg/l using an air-coal gas flame. Both SO_4^{-2} and PO_4^{-3} ions must be absent. A somewhat less sensitive method (5-500 μg/l) was also established based on the enhancement of zirconium absorption by fluoride in the nitrous oxide-acetylene flame. They also established an even less sensitive method (400 - 4000 mg/l) without interference based on the enhancement of titanium absorption. These methods offer the advantage of being rapid, and little handling of collected samples is required.

6.3.4.4 X-Ray Spectrography

An X-ray spectrographic method(4342) was established for measuring fluoride collected by nearly any of the previously described sampling methods, adjusting the pH of the solution containing the fluoride, and collecting the fluoride as LaF_3 on a Millipore disc with a pore size of 2μ. The disc is washed, dried and submitted to X-ray spectrographic measurement with a tungsten target and a lithium fluoride analyzing crystal. Fluoride can be detected in the range of 1μg to about 10 mg without interference.

6.3.4.5 Polarographic

MacNulty, et al,(535) applied to fluoride determination the reduction of the polarographic half-wave potential at 0.3V versus saturated-calomel electrode (pH 4.6 in acetate buffer) for the sodium salt of 5-sulfo-2 hydroxy-αbenzene - azo-2 naphthol in the presence of aluminum. Fluoride complexes aluminum and reduces the half-wave potential. The method can detect 0.2 μg/ml but the method precision and the maximum concentration of fluoride that could be detected was not investigated.

6.3.4.6 Radio Release

Carmichael and Whitley(4343) established a radio-release method for determination of fluoride (20 to 100 μg). The fluoride is converted to a zirconium salt, placed in a neutron flux, and the radioactivity release measured. The relative precision is about 5%; PO_4^{-3}, Fe^{+3} and Al^{+3} interfere.

6.3.4.7 Amperometric

A patent(4344) was issued for an amperometric method for fluorides from an air sample that was collected in 0.5 M nitric acid. The fluoride is determined by a platinum wire or plate electrode and a zirconium wire electrode rotating at 300 to 1600 rpm and maintained between -1 and +1 volt with respect to an S.C.E. The current passing between the electrodes was measured. The method can measure 0.05 μg - 1 μg/ml in the collecting solution. This method was not applied to detecting titration end-points, but could be considered.

6.3.4.8 Photo Activation

Kosta and Slunecko(4345) demonstrated the use of photo activation for determining fluoride in the concentration range of 0.01 to 5% on as little as 1160 μg of sample. The method has not been applied to gas stream fluorides, but could be used to determine the fluoride content of particulates collected on a filter. Interferences from elements such as chlorine, bromine, and sulfur can be eliminated or reduced to a minimum by adjusting irradiation time, waiting period, and energy of the primary electron beam. Results obtained were in good agreement with those obtained by distillation-titration methods.

6.3.4.9 Mass Spectrometric

Mass spectrophotometric analysis of anode gases from aluminum reduction cells was accomplished by Henry and Holliday(892) for HF, SiF_4, CF_4 and C_2F_6. The method determined the substances from 0.1 mol % to 100 mol %.

6.3.4.10 Electrochemical

Curran and Fletcher(4346) determined fluoride by precipitating fluoride ions with lanthanum ion electrochemically generated from lanthanum hexafluoride anode. The end-point was detected with a fluoride specific ion electrode.

Fluoride was determined by null point potentiometric measurement of the cerium (IV) cerium (III) reduction potential(4347) for solution containing greater than 14 μg of fluoride per ml of solution. The method can be applied to Willard and Winter distillates or ion exchange eluates.

A coulometric specific method was established by Kaye and Griggs(260) for free fluorine in a gas stream. In this method gas is aspirated at constant flow rates between 100 and 300 ml/min through 0.2 MLiCl. The fluorine oxidizes the Cl^- with one mole of fluorine corresponding to two atoms of Cl^-. The quantity of fluorine is determined coulometrically using a silver anode and a platinum gauze cathode. The method determines 0.1 ppm up to about 100 ppm of fluorine.

6.3.4.11 Gas Chromatography

The analysis of various fluorine containing compounds was investigated by Pappas and Million.(4348) They found the high affinity of HF toward almost any surface to be a problem. By the use of Teflon columns prepared with Teflon-6 support coated with fluorocarbon oil and carrier gas spiked with HF as proposed by Knight,(4349) they found that HF along with other fluorine compounds in the concentration range of 0.1 mol % to 100 mol % could be separated and measured with a gas density balance. Air was used as the carrier gas, but greater sensitivity than the ppm level they observed could be achieved with a carrier gas such as sulfur hexafluoride. More sensitive detectors have not been investigated.

6.3.4.12 Infrared Spectrometry and Infrared Lasers

Hydrogen fluoride has an absorption band at 3961.6 cm^{-1}, but this absorption band has not been used for determinations in the stack gases because of interactions with water vapor. SiF_4 has absorption bands at 1010 and 800 cm^{-1}. A recent review of infrared lasers for monitoring air pollution by Hanst(4350) proposed a method using a Kr laser and the infrared absorption line for HF.

6.3.4.13 Instrumented Methods Summary

With the exception of the specific ion electrode, the instrumental methods presented are useful for only special cases. Because the specific ion electrode is accurate when properly used and easy to use, the specific ion electrode is recommended for fluoride determination whenever possible.

6.3.5 Continuous and Semicontinuous Methods

There are at present no continuous or semicontinuous methods in use for the determination of the fluoride content of the various gaseous effluents from manufacturing processes and the abatement systems employed in connection with the processes. Most continuous or semicontinuous methods were developed for measuring fluoride content of the ambient atmosphere. These methods are summarized here because they can be considered as candidates for continuous monitoring of plant effluents.

The analysis of air for detecting fluorine compounds in the parts per billion concentration range is usually done by aspirating a large volume of air through distilled water or dilute alkali, concentrating the fluoride by distillation, ion exchange or diffusion (as discussed under titration and colorimetric methods), and then determining the quantities of fluorides by titrimetry or colorimetry. The distillation or ion-exchange step can be omitted only in special cases. Collection of enough fluoride for analysis may take several hours to one or two days, thus giving long term average concentrations. A method for continuous determination of fluoride content of process stream effluents is needed. The various approaches that have been developed are:

- Mini-Adak Colorimetric Analyzer
- Fluorescence-Quenching Method (SRI Fluoride Recorder)

- Billion-Aire Ionization Detector
- Current Flow Method
- Specific Ion Electrode Method

6.3.5.1 Mini-Adak Analyzer

In 1956, Adams, Darra and Koppe(4351) reported on a prototype photometric fluoride analyzer for use with a liquid reagent. In 1959, Adams and Koppe(691) studied this instrument extensively and established that there was an excellent correlation between the instrument and conventional sampling and analytical procedures for total soluble ion-producing fluoride pollutants. Basically, the instrument may be characterized as a recording flow colorimeter in which the flow forms an integral part of the air-reagent absorption system. As a fluoride analyzer, it photometrically measures and records the rate of reaction of zirconium-Eriochrome Cyanine R reagent with concentration of soluble fluorides in a sampled air stream throughout a given sampling period. High sensitivity is achieved by an unusual absorber which permits the contact of a small volume of liquid with a large volume of air (1 cu ft per min). The efficiency of hydrogen fluoride absorption is reported to be 95%. The volume of liquid is kept constant by automatic addition of water to replace evaporation losses. The liquid is periodically discarded and replaced by a measured volume of fresh solution. The addition of fluoride ion to the zirconium-Eriochrome Cyanine R reagent shifts the absorption maximum to 550 $m\mu$. The color is measured continuously by a recording colorimeter. Response of the recorder to fluoride is nearly linear at 1 scale division per μg of fluoride ion per 15 ml solution until 20 μg are added. In the range from 0.75 to 35 ppb hydrogen fluoride, the standard error of estimate was about 0.8 ppb.

6.3.5.2 Fluorescence-Quenching Methods (SRI Fluoride Recorder)

Chaikin and Associates at Stanford Research Institute developed a fluoride recorder(159,4353) which was further modified by Thomas, St. John, and Chaikin(2263,625) to provide an instrument that could operate under field conditions. The method consists of drawing parallel air streams into the analyzer through warmed glass tubes; one tube coated with $NaHCO_3$ and the other clean. The $NaHCO_3$ absorbs hydrogen fluoride, but the clean tube allows it to pass. The air streams are drawn through adjacent spots on sensitized paper tape made by dipping chromatrography paper in a methanol solution of 8-hydroxyquinoline and magnesium acetate. The resulting magnesium salt of 8-hydroxyquinoline fluoresces when illuminated with ultraviolet light. The visible fluorescence is quenched by hydrogen fluoride, thus providing a quantitative measure of fluoride. The difference in emitted light from the two areas of paper type is monitored by reflecting the two beams of light onto balanced photomultiplier tubes. Differential output from the tubes is recorded on a strip chart recorder. This instrument is 50 to 100 times more sensitive than the Adak recorder and determines only hydrogen fluoride, not total fluoride. The instrument can detect hydrogen fluoride in the range 0.2 to 10 ppb and appears free of interferences by common air pollutants. However, the instrument requires additional field testing.

6.3.5.3 Billion-Aire Ionization Detector

The Billion-Aire Ionization Detector manufactured by the Mine Safety Appliance Company(591) lends itself to the detection of hydrogen fluoride and fluorine in air. When a gas is ionized in the detector between two oppositely charged electrodes, a current is conducted depending primarily on the strength of the ionizing source, the applied voltage, and the composition and pressure of the gas. With air in the detection chamber, most gaseous additives in the concentration range of several thousand parts per million will cause only small changes in ion current. However, very small concentrations of finely divided particulate matter produce a pronounced decrease in current. The action of particles is to promote effective recombination through third body collisions and to decrease mobility through attachment. By converting a gas to particulate matter by a suitable reaction and measuring the decrease in ion current due to the presence of the particles in an ion chamber, many contaminants can be detected in the concentration of ppb. For example, HF, HCl and NO_2 can be converted to particulate aerosol by reaction with ammonia. Though the instrument is not specific for hydrogen fluoride, it provides instantaneous response for hydrogen fluoride and fluorine concentrations of 1 to 100 ppb.

6.3.5.4 Current Flow Method

Howard, et al(802) developed a portable fluoride analyzer based on the fact that the current from an aluminum-platinum internal electrolysis cell is a function of the fluoride content of an acetic acid electrolyte, after the sampled air has been scrubbed with the electrolyte. The analyzer responds to all substances which form fluoride ion in aqueous solution and is specific for fluoride in the presence of common contaminants. The method is capable of detecting from 5 to 100 ppb for a 2-liter sample.

A second electroanalytical instrument that detects fluorine but not fluorides was developed by Kaye and Griggs.(260) In this instrument, air containing fluorine exidizes Cl^- ion in a buffered LiCl solution in a solution containing platinum and silver electrodes. The chlorine formed is reduced at the silver cathode. Insoluble AgCl is produced on the cathode so that chloride is removed from the solution. For every molecule of fluorine, two electrons flow through the coulometric circuit and two atoms of chlorine are transformed from solution to cathode. By using a pump to deliver a constant flow of air to the instrument one can determine fluorine concentrations between 5 and 1000 ppm without interferences from other atmospheric oxidants.

6.3.5.5 Specific Ion Electrode Method

Light(4354) discussed the adaptation of the fluoride ion specific electrode to the continuous monitoring of gas streams. By simply scrubbing the gaseous constituents with a suitable reagent and measuring the quantity of gas, reagent solution, and concentration of the resulting solution with the electrode automatic monitoring can be achieved. Direct application of this technique to effluent gas analysis as yet has not been reported, but recently has been applied by Mori, et al(4381) to the determination of hydrogen fluoride in the atmosphere. The hydrogen fluoride is collected by absorption on dry sodium carbonate coated glass tubes. The sodium carbonate and collected fluorides are washed to a collection container, the solution buffered, and the fluoride concentration determined with the specific ion electrode. Automatic cycling of the apparatus provides a continuous recording of the hydrogen fluoride concentration of air.